ELEMENTARY
PHYSICAL CHEMISTRY
FOR B. Sc. STUDENTS

BY
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ELEVENTH EDITION

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Dedicated
To the memory of
MY BELOVED PARENTS

PREFACE

The present edition is a thoroughly revised and somewhat enlarged version of the eleventh edition. A special attempt has been made in this edition to correct the many numerical inaccuracies which had inadvertently crept in the worked out examples and exercises ; in this labour I have received ungrudging assistance from a few of my research associates, specially from Sri Tilak Guha, M.Sc. to all of whom my earnest thanks are due. Many of our Professors have helped me by offering suggestions and information and by pointing out mistakes, inaccuracies and incongruities to all of whom I am greatly indebted. On this account my special thanks are due to Dr. M. N. Das, D.Sc., Jadavpur, Prof. R. D. Sharma, Jodhpur, Prof. C. M. Gupta, Kota, Prof. M. S. Murdia, Udaipur, Prof. S. C. Bhattacharya, Midnapur, Prof. V. Gopalakrishnan, Annamalainagar, Prof. Y. V. Lawande, Bombay, Prof. P. S. Sastry, Bijapur, Prof Serajul Islam, E. Pakistan, and others. I hope the book will continue to render its humble service to the cause of science education in our country and neighbouring ones.

June 25, 1956
  I.A.C.S.
Calcutta-32

SANTI R. PALIT

PREFACE TO THE TENTH EDITION

In our country whose people are famed from dim antiquity to the present era for abstract reasoning, the incongruous fact remains that in both quality and quantity non-physical chemists have stolen a march over physical chemists. And, though the standard of teaching has vastly improved during the last decade or so, the lamentable fact is that in many Universities a set of old stock questions hardly doing any justice to present-day Physical Chemistry supplies almost all the materials for the question papers. As a result, most students put only a half-hearted effort to learn the subject as a connected whole. The malady is accentuated by the appearance of a few so-called text books which are merely note-books on selected topics, very often full of mistakes, fallacies and misstatements. This situation is fraught with grave consequences on a national level.

The present edition is an uncompromising attempt to counter the above lapse in the nation's chemical education by producing a well-knit text-book, though on a very elementary level, exposing the elegance, subtlety and logical pattern of the Science of Physical Chemistry with the simplicity and clarity of presentation for which the previous editions were noted. This elementary book would therefore help the students to learn the subject as a scientific discipline and also to face the University degree exami-

nations confidently. With a view to this, extensive additions have been made and at many places the book has been recast, rewritten and reoriented, with the hope that this would be altogether for the better.

In this major remodelling of the book I have been helped by suggestions from many Professors, my debt to whom is a pleasure to acknowledge. I specially thank Prof. P. V. Appu, Palghat, Prof. M. Bhale, Indore, Prof. C. M. Desai, Ph.D., Indore, Prof. K. K. Dole, Ph.D., Poona, Prof. J. N. Gaur, Ph.D., Jaipur, Prof. A. N. Halder, Bankura, Prof. D. Krishnamurty, Bikaner, Prof. V. V. Narasimha Rao, Guntur, Prof. M. L. Pai, Ph.D., Baroda, Prof. B. B. Palit, Contai and Prof. R. P. Shukla, Ph.D., Indore ; and also Prof. A. K. Bhattacharya, D.Sc., Agra, Prof. D. K. Bose, Calcutta, Prof. P. K. Banerjee, D.Phil., Calcutta and Prof. R. S. Saxena, Ph.D., Rajasthan, for estwhile suggestions.

It is earnestly hoped that the present edition prepared with the cream of experience of so many, would continue to enjoy the support and patronage of Professors of Physical Chemistry throughout the country as it has been privileged to do in the past.

*Indian Association for
the Cultivation of Science
Calcutta-32, July 12, 1956* } S. R. PALIT

Extract from the
PREFACE TO THE FIRST EDITION

My aim in writing the present volume has been to place before the students the fundamental ideas of theoretical chemistry on up-to-date lines in as simple and clear a manner as possible and to explain lucidly the methods by which these abstract ideas are made to bear upon actual problems of physical chemistry. The book is primarily intended for the students preparing for the Bachelor's degree course in pass standard of Indian Universities and . . . I have always had in my mind an intention to evoke in the students an interest for the subject and not make it only a cram-book for examinations.

My object has not been so much to give a complete presentation of each subject up to the last word on it as to explain thoroughly the elementary principles and their applications. I have worked out numerous problems which, I am sure, will prove helpful even to the Honours students.

I must avail myself of this opportunity of expressing my indebtedness to the authors of some well-known books on the subject which I have freely consulted and to my friends, well-wishers and colleagues, but for whose kind help and co-operation it would have been impossible to bring out the book.

VIDYASAGAR COLLEGE
June, 1, 1938
Calcutta. } S. R. PALIT

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CHAPTER I

INTRODUCTION

Growth of Science—In the workhouse of imagination reason moulds experience into science. Human experience as such never constitutes a science but is merely a loose collection of facts and though important is hardly interesting by itself. Men as thinking and speculative beings attempt to order these into a satisfying pattern clearly highlighting the coordination and correlation among the various sets of facts, and the resulting coordinated pattern of knowledge is science.

The individual human wit being very meagre in its scope and the heritage of collected facts growing bigger and bigger from generation to generation, science divides and subdivides itself into intermerging branches and sub-branches in its onward march. The line of demarcation between two divisions of science being necessarily hazy and conventional, border-line subjects where interests overlap and which can stand as a common meeting place, naturally come into being.

Physical Chemistry as a Scientific Discipline—Physical Chemistry is one such border-line subject where rigours of mathematical reasoning and the lofty imagination of physicists are welded together to illuminate varied chemical phenomena with telling and beautiful results. Like any other branch of scientific knowledge, its advances have been made through synthetic as well as analytic approaches, through framing of theories and hypotheses, through strict deduction and soaring imagination, the expediency dictating the method used. So, its main objective is to arrive at an understanding of chemical phenomena and facts by following strictly scientific methods.

Law, Hypothesis and Theory —From observations and experiments facts accumulate, and from this collection of facts one, in the course of sorting out similar facts, finds out some generalisation valid for a group of these facts. If this generalisation can embrace a large number of facts and is not found failing in a single case so far tried, it is termed a *Law*. The law of conservation of mass is truly a law for within its scope it has always been found to be true.

There is another scientific method, often used, which has contributed much towards the development of science. This is the framing of hypothesis. An imaginary model is framed so that the expected property of the model corresponds to the known property of the system under investigation. Such a bold conjecture constitutes a *hypothesis* and taking for granted the truth of a hypothesis, facts are explained on its basis.

A hypothesis, though of a speculative origin, should on no account be regarded as a drill of imagination only. On the other

hand, it has been most fruitful and illuminating in the pursuit of science. It suggests new experiments to test its own validity and opens up newer avenues of research. If further experiments reveal the insufficiency of a hypothesis, it is either to be rejected or modified but whatever may be the result, lasting gain always accrues to science for, by this means we have been able to add fresh stocks to our store of knowledge. So, a hypothesis is always on probation only, and on the first failure should be substituted or modified, without any consideration of its past service. "Accordingly, a hypothesis is not the end but rather the means of attaining the end."

When a hypothesis is found to be in harmony with all the known facts in a given field, it is promoted to the rank of a *theory*. The distinction between a theory and a law is that a theory often involves detailed consideration about the structure of matter whereas a law is just a summarising statement on the behaviour of nature.

Main Streams of Physical Chemistry—There are two general problems which are most fundamental to physical chemistry and the major portion of the efforts of physical chemists is spent on them. They are the problems of chemical equilibria and chemical kinetics. In other words, our primary concern is a knowledge about where the equilibrium position will be in a given chemical reaction and how fast that equilibrium will be attained. Following the high road of thermodynamics a satisfactory solution of the first problem has been, at least in principle, achieved, whereas a good start has of late been made towards the solution of the technically important second problem. Besides these, the detailed knowledge of atomic structure as revealed by physicists has been very ably used by physical chemists to understand the most basic problem in chemistry, viz., how and why atoms combine.

These subjects along with some introductory matter and some less fundamental but often practically more important topics would be our subject of study in the present book on a very elementary level.

CHAPTER II

THE IDEAL GAS AND ITS KINETIC-MOLECULAR THEORY

The Nature of Gases— A gas may be defined as a homogeneous substance whose volume increases without limit when the pressure on it is continuously reduced, the temperature being maintained constant. Gases are further characterised by the property that when different gases in any proportions whatever are brought into contact they diffuse rapidly into each other and form a homogeneous mixture.

In contrast with solids and liquids, gases are characterised by low density and high compressibility. Generally speaking, under ordinary conditions *gases are about one thousandth as dense as liquids.* In point of compressibility, however, the difference is much marked, liquids being about one hundred thousand times less compressible than gases.

It should be clearly emphasised at the outset, as is to be proved later (Ch. V) that there is no sharp dividing line between the liquid and the gaseous state and in certain modes of transition it is very difficult to say where one state ends and the other begins.

The Gas Laws— A very striking fact about gases is that, independent of their chemical nature, they approximately obey certain very simple laws with regard to their physical properties. There are three laws regulating the pressure, volume and temperature of any gas, which are enunciated below:—

1. **Boyle's Law** (1662)—*Temperature remaining constant, the volume of a given mass of gas is inversely proportional to the pressure i. e.* expressed algebraically, $P \propto \dfrac{1}{V}$ or $PV = constant$

(at constant temperature).

2. **Charles' Law** (1787) *or* **Gay Lussac's Law** (1802)— *Pressure remaining constant, all gases expand or contract by the same fraction of its volume at zero degree centigrade per degree change in temperature.* In other words, the increase in volume per unit volume per degree rise in temperature is constant and equal for all gases.

Hence if V_0 and V are the volumes at $0°C$ and $t°C$ respectively,

$$(V - V_0)/(V_0 \times t) = \text{constant, say, } \alpha.$$
$$\text{or } V = V_0(1 + \alpha t)$$

Now α has been experimentally found to be equal to $1/273.1$.

$$\therefore \quad V/V_0 = (273.1 + t)/273.1$$

If we define a new temperature scale and let it start from minus $273.1°C$ and call this absolute scale of temperature, denoted by T, we have

$$V/V_0 = T/T_0 \quad \text{or} \quad V_2/V_1 = T_2/T_1$$

Hence Charles' law may be alternatively stated as follows: *Pressure remaining constant, the volume of a given mass of gas is directly proportional to the absolute temperature.*

3. *At constant volume, the pressure of a given mass of gas is proportional to the absolute temperature, i.e.* expressed algebraically $P \propto T$ or $P/T = const.$ *(at constant volume).*

The above three laws are not independent, and given any two, the other one can be very simply deduced.
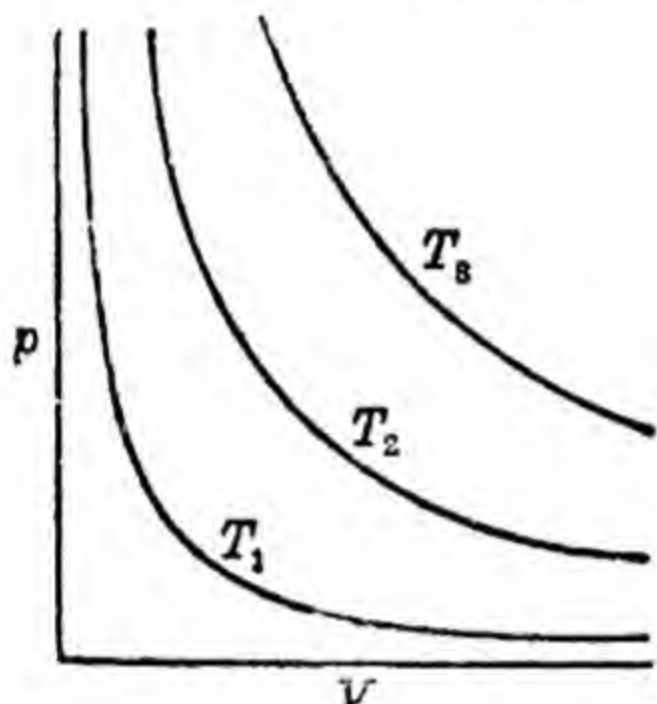
Fig. 1—Isothermals of Ideal Gases (Boyle's Law); $T_3 > T_2 > T_1$.   Fig. 2—Isobars of Ideal Gases (Charles' Law); $P_3 > P_2 > P_1$.
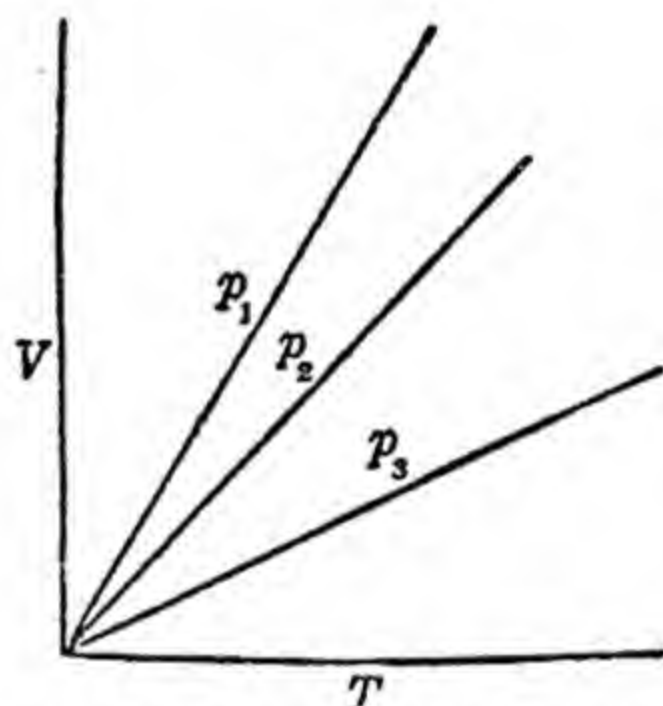
Boyle's law is graphically represented on squared paper, by plotting pressure against the volume. The curves obtained are called *isothermals* and are of the rectangular hyperbola type (Fig. 1). Similarly, Charles' law is graphically represented by plotting volume against absolute temperature when we get straight lines inclined to the axes and passing through the origin indicating that the volume of a gas theoretically vanishes at absolute zero (Fig. 2). Curves in Fig. 1 are called *isothermals* since they represent the behaviour of gases at constant temperature, and curves in Fig. 2 are called *isobars* since they refer to gases at constant pressure (*iso* = same, *bar* = pressure).

Combination of Boyle's and Charles' Laws— The gas laws can be summarised in a single equation by well known methods of algebra as follows:

Let P = pressure, V = volume and T = absolute temperature of m mass of a gas.

V varies as $\frac{1}{P}$ when T is constant (Boyle's law).

and V varies as T when P is constant (Charles' Law).

So, V varies as $\frac{1}{P} \cdot T$, when all of them vary.

Or, $V = constant \cdot \frac{T}{P}$ or, $\frac{PV}{T} = constant = k$

Or, $PV = kT$

i.e. the product of pressure and volume of any gas is proportional to the absolute temperature.

Ideal Gas Equation—At any given pressure and temperature, the volume of a gas is proportional to the amount of gas present and so the value of k in the foregoing equation is proportional to the amount of the gas taken. Now, according to Avogadro's hypothesis, a gram-molecule commonly called *mol* (molecular weight expressed in grams) of any gas occupies the same volume under the same conditions of temperature and pressure, and so, the value of the constant, k is the same for one gram molecule of *all gases*, independent of the conditions under which the gases are measured. This value of the constant, k referred to per gram molecule, is usually represented by R and is called the *molar gas constant*. The equation then assumes the familiar form:

$$PV = RT \qquad \qquad \dots \text{(1)-II}$$

where V is the volume of *one gram-molecule* of any gas, under a pressure P and at an absolute temperature T ; equations such as these correlating the pressure, volume and temperature are called equations of state and so the above equation is called the *equation of state* of an ideal or perfect gas.

The equation of state of an ideal gas, PV=RT is applicable to one gram molecule (henceforth to be called **MOL**), but if there are present 'n' mols of a gas the equation assumes the form PV=nRT, since the volume will be n times multiplied and so the right hand side is to be multiplied by n. If there are present 'g' gms of a gas of molecular weight M, then evidently the number of mols, $n = g/M$ and therefore, $PV = \frac{g}{M}RT$. The following are the three alternative forms of the equation of state of a perfect gas:—

(i) **PV = RT** ... *valid for one mol.* ... (1)-II

(ii) **PV = nRT** ... *valid for any amount* ... (2)-II

(iii) **PV = $\frac{g}{M}$RT** ... *-do-* ... (3)-II

A similar equation is applicable also to gas mixtures (*vide,* Ch. VIII).

In the above equations, P and V may be expressed in any system of units with a corresponding change in the unit and numerical value of R, but T is to be always expressed in absolute scale.

Ideal Gas Equation and Real Gases.—The ideal gas equation, PV=RT, is an idealised equation, which is not obeyed by a single gas over an extensive range of temperature and pressure. It is at best a representation of the average behaviour of real

gases under ordinary conditions, and is a code of conduct which we hope all well-behaving gases should aim to follow.

PV per Mol in c.c.-atmos. at N.T.P. for some Common Gases

Perfect gas	... 22.415	Argon	... 22,390
Hydrogen	... 22,432	Chlorine	... 22,063
Helium	... 22,396	Carbon dioxide	... 22,263
Nitrogen	... 22,403	Ethane	... 22,172
Oxygen	... 22,392	Ethylene	... 22,246
Ammonia	... 22,094	Acetylene	... 22,085

The PV-values for a few real gases at N.T.P. as collected in the above table, clearly show that this value is not exactly the same for all gases. Hydrogen occupies a slightly higher volume than that of a perfect gas and the other gases occupy a little less volume. The most significant fact, however, is that *this value is exactly the same for all gases at sufficiently low pressure and is equal to RT*. In plain words, whatever may be the value of PV of *any gas*,—it does not matter whether it is higher or lower than the perfect gas value—this value would change with lowering of pressure to ultimately attain the perfect gas value and further reduction of pressure would leave this value unaffected. So, the ideal gas equation may be regarded as a limiting law valid for all gases under the limiting conditions of zero pressure. However, for many purposes, specially at moderate pressures and away from its condensation temperature, we shall be using the ideal or perfect gas equation to describe the behaviour of real gases because the perfect gas approximation is good enough for our purpose for such applications.

Modified Form of the Ideal Gas Equation—The general gas equation is sometimes modified to correlate density.

$$PV = \frac{g}{M} RT, \qquad Or, \ P = \frac{g}{V}\frac{RT}{M} \ Or, \ P = d\frac{RT}{M} \qquad [8.II]$$

$$\left[since \ d = Density = \frac{mass}{volume} = \frac{g}{V} \right]$$

Or, for any given mass of gas at constant temperature, pressure varies directly as the density, i.e. P ∝ d = const. This form of the gas equation is very suitable for application to gases with non-uniform pressure, for example, a gas in a gravitational field.

Dimensions of the Molar Gas Constant, R—The gas constant, R is not an abstract number but has the dimensions of energy per degree per mol, and its numerical measure will therefore vary in different systems of unit. That R has the dimension of energy divided by temperature may be proved as follows. For one mol of a perfect gas, we have

$$P = \frac{PV}{T}$$

Now P = Pressure = force per unit area = dyne cm⁻² and V = Volume = cm³ mol⁻¹

So, R = ...

Alternatively, $R = \dfrac{dynes \times cm^3}{cm^2 \times temp.}$ per mol. $= \dfrac{dyne \times cm}{degree}$ per mol. $= \dfrac{erg}{degree}$ per mol.

$$= energy\ per\ degree\ absolute\ per\ mol.$$

and since energy can be expressed in different systems of units as ergs, calories, etc. R will also have different values in these different systems as calculated below.

VALUES OF R

(a) **R in C. G. S. Unit**—From the experimentally observed fact that a gram-molecule of any gas occupies 22·4 litres at N.T.P., R is calculated as shown below—

Normal pressure = 76 cm. of mercury

$$= 76 \times 13·6 \times 981\ dynes\ per\ sq.\ cm.$$

[Density of mercury = 13·6 and g = 981 C.G.S. units.]

$$\therefore\ R = \frac{PV}{T} = \frac{76 \times 13·6 \times 981 \times 22·4 \times 1000}{273}\ per\ mol.$$

$$= 8·3162 \times 10^7\ ergs\ per\ degree\ per\ mol.$$

$$= 8·3162\ joules\ per\ degree\ per\ mol$$

[Since, 1 Joule = 10^7 ergs]

(b) **R in Litre-atmosphere**—If pressure is expressed in atmospheres and volume in litres,

$$R = \frac{1 \times 22·4}{273} = 0·082\ litre\ atmosphere\ per\ degree\ per\ mol.$$

(c) **R in Calories**—

Now $R = 8·32 \times 10^7$ ergs per degree per mol.

But 1 calorie $= 4·18 \times 10^7$ ergs

(Mechanical equivalent of heat).

$$\therefore\ R = \frac{8·32 \times 10^7}{4·18 \times 10^7} = 1·987\ calories\ per\ degree\ per\ mol.$$

$$= (nearly)\ 2\ cals.\ per\ degree\ per\ mol.$$

(d) **R in Engineering Units**—The value of R in foot-pounds per degree can be easily calculated from the known fact that one pound-mol (molecular weight expressed in pounds) of any gas at N.T.P. occupies 359 cubic feet.

$$\therefore\ R = \frac{PV}{T} = \frac{2116·8 \times 359}{273} = 2783\ ft.\ lb/degree\ per\ mol.$$

[since 1 atmosphere = 14·7 lbs. per sq. in.

$$= 14·7 \times 144 = 2116·8\ lbs.\ per\ sq.\ ft.]$$

EXAMPLE 1. How many pounds of carbon monoxide are contained in a vessel of capacity 1000 cu. ft. at three atmospheres pressure and 0° C.

$$PV = \frac{g}{M} \times RT\ \ or\ \ g = \frac{M.\ P.\ V.}{R.\ T.}$$

$$\therefore\ g = \frac{(28) \times (3 \times 14·7 \times 144) \times 1000}{(2783) \times (273)} = 234·04\ lbs.$$

The chemical engineers often use degree Fahrenheit and a proportionate absolute scale (degree Rankine) in their calculations but the above example is sufficient to show the nature of such calculations. For rapid approximate engineering calculations the student should do well to remember that 2·8 lb-mols of any gas are contained in 1000 cu. ft. at N.T.P., i.e. a 1000 cu. ft. gas reservoir at N.T.P. contains 2·8 times the pound-mol of a gas.

VALUES OF R IN DIFFERENT UNITS

$R = 8\cdot31 \times 10^7$ *ergs per degree absolute per mol*

$\quad = 8\cdot31$ *Joules per degree absolute per mol*

$\quad = 0\cdot0821$ *litre-atmosphere per degree absolute per mol*

$\quad = 82\cdot1$ *cc-atoms per degree absolute per mol*

$\quad = 1\cdot99$ *calories per degree absolute per mol*

N.B. The student should commit to memory at least one of the values of R and it is best to remember it as 0·0821 litre atmosphere per degree per mol. Sums in this book have been worked out on this basis. The student should also note that very often the units are given in algebraic notation; for example, the last value of R then appears as $1\cdot99$ calories degree^{-1} mol.$^{-1}$.

The most precise value of R, the universal gas constant as given by U. S. National Bureau of Standards is $1\cdot98718 \pm 0\cdot00013$ calories per degree or $8\cdot31298 \pm 0\cdot00054$ International Joules per degree.

KINETIC MOLECULAR THEORY OF IDEAL GASES

Basic Postulates of the Kinetic Theory— Since gases, in general, obey such simple laws, attempts were made to explain the behaviour of gases from a mechanical model. This model which is the outcome of the labours of Maxwell, Boltzmann, Clausius and others mainly during 1860-90 is known as the kinetic theory of gases.

The theory was put forward before the structure of matter was understood but nevertheless it has been extremely useful as a theoretical basis for interpreting the properties of gases. The fundamental postulates of the kinetic theory are the following :—

(a) The kinetic theory assumes that a gas is made up of an exceedingly large number of minute particles (the molecules of atomic theory) all having the same mass. The molecules are supposed to behave like solid, spherical and *perfectly elastic* particles having no attraction for each other.

(b) The molecules are moving at random in straight lines with high velocities undergoing elastic collisions with each other and against the walls of the containing vessel. The pressure exerted by a gas is due to the continuous bombardment on the walls of the containing vessel by the gas molecules as a result of their chaotic motion.

Obviously, the collisions among molecules themselves and the walls will be greater in number when the volume is decreased, as, then there

is less room for motion; this explains why the pressure gets increased when the volume is decreased.

(c) The molecules are themselves of a very small dimension, their actual volume being negligible in comparison with the space at their disposal i.e. the volume of the vessel.

This is easily seen to be true now in retrospect from the now known diameter of gas molecules. Thus, the ordinary common gases have diameters in the range, 2 to 5A [A = one Angström unit = 10^{-8} cm] which is evidently negligible in comparison with the dimensions of the containing vessels.

Gas Laws from Kinetic Theory —Let us imagine a certain quantity of a gas to be confined in a cube (Fig. 3) the length of whose side is l. Let the total number of molecules be n and let each of them have a mass equal to m. The molecules are moving at random with different speeds the average of which is c (c is called the root-mean-square-speed, vide P. 12). Since the average speed is c we may regard that all molecules are moving with the same velocity c in all possible directions and let us calculate the effect produced on each wall. Concentrating our attention upon a particular molecule, we can resolve its velocity c into three components u, v and w at right angles to one another and parallel to the sides AB, AC and AD of the containing vessel.

The component u parallel to AB, has effect only on the wall $ACED$ and the wall opposite to it; it has got no effect on the other walls. The molecule strikes with the velocity u and rebounds with the same velocity, since the walls and the molecules behave like perfectly elastic solids. So, the momentum before collision in the direction AB is mu and after collision in the same direction is $-mu$ (Fig. 4).

Hence, the change of momentum per collision = original momentum – final momentum = $mu - (-mu) = 2mu$.
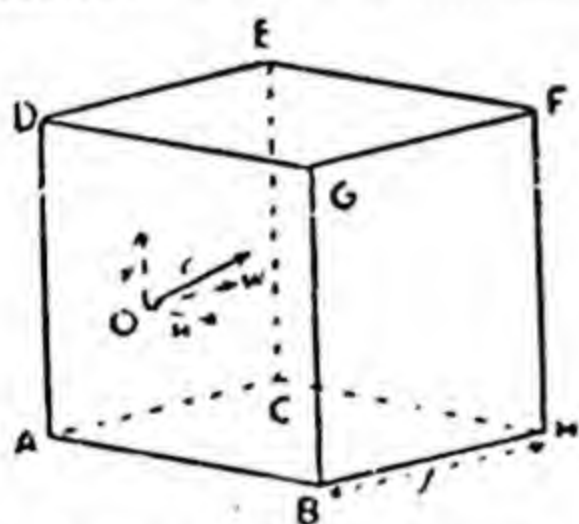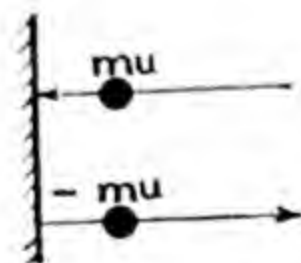

Fig. 3—Kinetic Theory Deduction.

Fig. 4—Change of momentum on rebound from wall.

If the distance between two opposite walls be l cm, the particle suffers one collision after each l cm; therefore, the total number of collisions per sec. = $\frac{u}{l}$. So, the total change of momentum per sec. due to the component u is $\frac{2mu^2}{l}$.

Similarly, the change of momentum per second for the other two components v and w are $\dfrac{2mv^2}{l}$ and $\dfrac{2mw^2}{l}$ respectively. Therefore, the total change of momentum in one second per

$$\text{molecule} = \frac{2m}{l}(u^2+v^2+w^2)$$

$$= \frac{2mc^2}{l} \text{ (Since, by dynamics, } c^2=u^2+v^2+w^2)$$

If there are n particles present, the total effect on the walls will be multiplied n times. Therefore, the total change of momentum for all the particles per second is equal to $\dfrac{2mnc^2}{l}$.

But, according to the second law of motion, we know that the rate of change of momentum is the impressed force. Now the impressed force *i.e.* the total pressure on the six walls of the cube is equal to $p \times 6l^2$, where p is the pressure per unit area and l^2 is the area of each face.

$$\therefore \ 6l^2 p = \frac{2mnc^2}{l} \text{ or } p = \frac{mnc^2}{3l^3} = \frac{mnc^2}{3v} \text{ (Since } l^3 = volume).$$

$$\text{Or } pv = \tfrac{1}{3}mnc^2 \qquad \ldots \qquad \ldots \qquad \ldots \quad (5)\text{-II}$$

The above deduction though made for a cube is valid for a vessel of any shape, for, the later may be imagined to be partitioned into a large number of infinitesimally small cubes, the total volume of which is equal in the limit to the volume of the particular vessel. The equation (5) is then valid for each cube, but the pressures on opposite sides of the common wall neutralise each other and the only surface left on which the gas pressure acts, is the outward surface of the exterior cubes, which in the limit is equal to the surface of the containing vessel.

Root-Mean-Square Speed—In the above deduction, the speed c has been for simplicity called the average speed but really it is not the average speed but is the root-mean-square (r. m. s.) speed. The latter is defined as *the square root of the mean value of the squares of the velocities of all molecules.* If there are say, two molecules moving with velocities 1 and 7 cm per sec. respectively their average speed is only 4 but their r.m.s. speed is the square root of $\frac{1}{2}(1^2+7^2)$ *i.e.*, 5. The reason that r.m.s. speed is to be used in the above calculation rather than the average speed, $\bar{c}$ is owing to the fact that the total kinetic energy with which we are essentially concerned in the above calculation is simply related by the usual equation to the square of the r.m.s. speed, c but not so to the average speed, $\bar{c}$. Thus, in the above example of two molecules having speeds of 1 and 7 cm. per sec. respectively, the total kinetic energy is $[\tfrac{1}{2}m1^2+\tfrac{1}{2}m7^2]=2\times\tfrac{1}{2}m5^2=$ No. of molecules $\times \tfrac{1}{2}m$ (r.m.s. speed)^2. In other words, the total kinetic energy of a mol of gas is $\tfrac{1}{2}Mc^2$, and not $\tfrac{1}{2}M\bar{c}^2$.

Hence, if n molecules have speeds c_1, c_2, c_3, c_4,.............c_n respectively, the average speed, $\bar{c}$ and the r.m.s. speed, c are given by the equations,

$$\text{Average Speed, } \bar{c} = \frac{c_1 + c_2 + c_3 + \cdots + c_n}{n}$$

$$\text{and R.M.S. Speed, } c = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \cdots c_n^2}{n}}$$

The r.m.s. speed, c may thus be defined as the hypothetical velocity which all the molecules of a gas would possess if the total kinetic energy was equally divided among them.

(a) **Deduction of Boyle's Law**—From eqn. (5), $pv = \frac{1}{3} mnc^2$, we find that for a given amount of any gas at a particular temperature, the right-hand side is a constant, since m and n are evidently constants and c also is constant at a constant temperature, for, an increase in c implies an increase in the total energy of the particles, which is not possible unless heat is supplied from outside.

Therefore, at a constant temperature, $pv = $ constant, which is Boyle's Law.

(b) **Deduction of Charles' Law**—Since an increase in temperature by applying heat from outside must increase the kinetic energy of the particles, it is assumed that the mean *translational* kinetic energy of a particle is a measure of the temperature of a gas and is proportional to the absolute temperature, T *i.e.* kinetic energy $\propto$ T = const. × T

Now $pv = \frac{1}{3} mnc^2 = \frac{2}{3} n (\frac{1}{2} mc^2)$

$pv = \frac{2}{3}$ Total Kinetic Energy = constant × T.   ... (6)-II

This is Charles' law.

Kinetic Energy of a Gas Molecule—Equation (6) can be easily put in the following forms which clearly bring forth the relationship between molecular kinetic energy and temperature.

$$\text{Total kinetic energy} = \frac{3}{2} RT \qquad \cdots \qquad \cdots \quad (7)\text{-II}$$

Since kinetic energy of translation can be resolved into three directions, which is expressed by saying that it has three *degrees of freedom*, we have

$$\left.\begin{array}{l}\textit{Kinetic energy per mol}\\ \textit{per degree of freedom}\end{array}\right\} = \frac{1}{2} RT \qquad \cdots \quad (8)\text{-II}$$

$$\therefore \left.\begin{array}{l}\textit{Kinetic energy per molecule}\\ \textit{per degree of freedom}\end{array}\right\} = \frac{1}{2} \frac{RT}{N} = \frac{1}{2} kT \quad \cdots \quad (9)\text{-II}$$

where $k (= R/N)$ is called the *Boltzmann constant*. This is in its simplest form one of the most, if not the most, profound relation in physical chemistry.

Since the average kinetic energy per molecule for *all* gases at the same temperature is the same, it is easy to prove from equation (5) that the *pressure of a gas is directly proportional to the number of molecules per unit volume at any given temperature.* This is a very important relation and signifies that all molecules, big or small, exert the same pressure at any given temperature independent of its chemical nature. This is rather surprising that a uranium hexafluoride molecule though one hundred and seventy six times heavier than a hydrogen molecule, exerts the same pressure. This paradox is easily understood if we remember that all molecules have exactly the same average kinetic energy of translation at the same temperature.

It should be noted that a molecule may have other types of kinetic energy besides translational kinetic energy, for example, the molecule may also rotate or vibrate, and so may have rotational or vibrational kinetic energy, but only the translational kinetic energy is a measure of its temperature, and indeed is proportional to absolute temperature.

(c) **Deduction of Avogadro's Law**—Suppose we have any two gases at the same temperature, volume and pressure. For the first gas, let the mass of each molecule and the total number of molecules be m_1 and n_1 respectively, and for the second gas let the corresponding values be m_2 and n_2. Since the two gases are at the same temperature, the mean kinetic energy for each particle is the same, i.e.

$$\tfrac{1}{2}m_1c_1^2 = \tfrac{1}{2}m_2c_2^2 \text{ or } m_1c_1^2 = m_2c_2^2.$$

Now, $pv = \tfrac{1}{3}m_1n_1c_1^2 = \tfrac{1}{3}m_2n_2c_2^2.$

Dividing one equation by the other, we get $n_1 = n_2$, i.e. *the number of molecules in equal volumes of all gases under the same conditions of temperature and pressure are equal,* which is Avogadro's hypothesis.

(d) **Deduction of Graham's Law**— The rate of diffusion of a gas through a porous vessel is evidently proportional to the speed of the molecules.

∴ Rate of diffusion = Mean speed, c.

But from eqn. (1), $c = \sqrt{\dfrac{3\,pv}{mn}} = \sqrt{\dfrac{3p}{d}}$, where d = density

[Since $\dfrac{mn}{v} = \dfrac{\text{mass}}{\text{volume}} = \text{density}$].

∴ Rate of diffusion $\propto \dfrac{1}{\sqrt{d}}$, which is Graham's law of diffusion (for a more detailed discussion of Graham's law see P. 17).

(e) **Mean Speed of a Gas Molecule**—Since, in the equation $pv = \tfrac{1}{3}mnc^2$ all quantities are known except c, it can be easily calculated. Let us calculate the speed of an oxygen molecule

at N.T.P. ($R = 8.313 \times 10^7$ ergs per degree). From the above equation we have,

$$c^2 = \frac{3pv}{M} \quad \text{or} \quad c^* = \sqrt{\frac{3pv}{M}} = \sqrt{\frac{3RT}{M}} \qquad \qquad \cdots \qquad \cdots \quad (10)\text{-}II$$

$$\therefore \quad c = \sqrt{\frac{3 \times 8.313 \times 10^7 \times 273}{32}} = 46,000 \text{ cm. per sec.}$$

So, a molecule of oxygen moves with a speed greater than a quarter of a mile per second, *i.e.* about 1000 miles per hour. In other words, the speed of a gas molecule under ordinary conditions is of the order of the velocity of sound, or of that of very fast jet-planes. It should be noted that the speed of a gas molecule is independent of pressure and has the same value for all molecules at equal T/M. Such high speeds of gas molecules explain why a gas occupies the whole available space in any container even against gravity, as it is clear that such a huge number of molecules with such enormous speed moving in a chaotic manner *i.e.* in all possible directions, would uniformly and completely fill all the available spaces of the container.

It would appear from this enormous speed of a gas molecule that any gas say, a good scent will make itself felt almost instantaneously at the other end of a room, which is never the case. The explanation is to be found in the fact that a molecule experiences an enormous number of collisions in its passage from one point to another at all possible angles and so the actual path traced out by a molecule is extremely zigzag and many times greater than its *net* displacement.

A very simple experiment can demonstrate the above points as also that molecules move in straight lines. The diagram (Fig. 5) is self-explanatory. That the iodine is deposited only on the opposite side in the evacuated system demonstrates the linear motion of gas molecules, whereas in the other case chaotic collisions with the molecules in air lead the iodine molecules astray from the straight path as discussed in the previous para and get them deposited all over the surface.
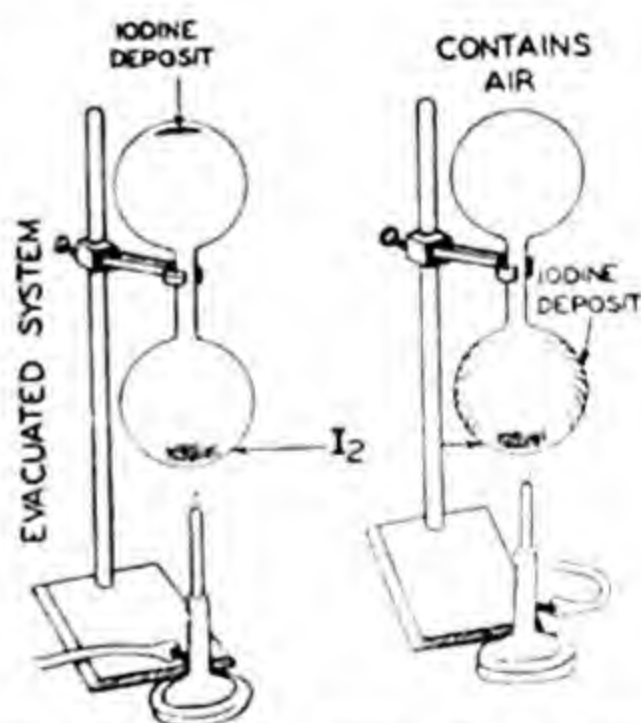
Fig. 5—Experimental demonstration of linear path of gas molecules.

Mean Free Path— The average distance travelled by a gas molecule between two consecutive collisions is called its *mean free path*. In order to have an idea of the numerical order of

* This speed is the r.m.s. speed (P. 13). The average speed, $\bar{c}$ is slightly less than c; in fact, it is given by the same expression where the factor 3 has been replaced by $8/\pi$.

the quantities involved, it may be noted that CO_2 gas which is about 4Å in diameter has a mean free path of about 500Å and N_2 molecule having a diameter of about 3·5Å has a mean free path of about 750Å under ordinary conditions. It is thus seen that a gas molecule moves more than one hundred times its diameter on the average in between two consecutive collisions.

Molecular Kinetic Picture of a Gas— We can have a fairly clear mental picture of an ordinary gas say, oxygen or carbon dioxide at N.T.P. The diameter of the molecules is about 4Å and the average distance of any molecule from its nearest neighbour is about 40Å. The molecules are moving with an average speed of about 40,000 cm per second and they hit another molecule after moving an average distance (mean free path) of about 500Å ; so a molecule passes by many molecules before it undergoes collision with one of them. The number of collisions undergone by a molecule per second, which is simply its speed divided by its mean free path, is thus seen to be a few billions (8×10^9) per second.

(f) **Distribution of Molecular Velocities—** As already pointed out all the molecules in a gas do not move with the same velocity but all velocities from very low to very high values are present in a gas at any instant. The reason for this is that granting all molecules to have equal speeds to start with, collisions between molecules take place at all possible angles leading to an unequal distribution of velocities. Maxwell first carried out rigid mathematical analysis of the problem and deduced quantitative values for such distribution. The results are shown graphically in the accompanying figure (Fig. 6) for oxygen at 0° and 100°C. For any velocity, c the ordinate at c represents the fraction of the total number of molecules having velocities between c and c + dc, where dc is an infinitesimal increment of c. It will be noted that very few molecules have zero or very high velocities, and at any temperature there is a most probable velocity (the maximum in each curve) and most of the molecules tend to have velocities near to this peak value. Further, the lower the temperature, the steeper is the distribution curve and also lower is the most probable velocity.

Velocities of molecules, c in cm/sec. $\times 10^4$

Fig. 6—Distribution of velocities in oxygen.

Suppose we want to know the fraction of the molecules which has speeds between say, 50,000 and 60,000 cm per sec. This is simply obtained by drawing two ordinates at the above two given speeds; the ratio of the area between these two ordinates under the curve to the total area under the curve gives the required fraction. Let us say that the value of this fraction is one-third. This means that at any instant one-third of the total number of molecules have speeds within the range 50,000 to 60,000 cm per sec. and all other molecules have either higher or lower speeds. Suppose at any instant we could take the above group of molecules which is one-third of the total number and in order to distinguish them from the rest, colour them red. At the next instant or at any later time, these "red" molecules will not necessarily be within the above velocity limit of 50,000 to 60,000 cm per sec. but will have all possible values. However, still the total fraction of the molecules within the above speed limit will be one-third of the total number because as many "red" molecules would have come out of the above range as would have entered it. In other words, the "complexion" of the system viewed as a whole remains constant though each molecule individually takes all possible speeds over a sufficiently long interval of time.

Diffusion and Effusion of Gases—Graham (1833) studied the rate of diffusion of gases through porous membranes such as unglazed porcelain, compressed graphite, etc. and arrived at the following law for the rate of diffusion of different gases:—*The rate of diffusion of any gas is inversely proportional to the square root of its density (Graham's law of diffusion)*. In other words, a gas weighing say, 4 gms per litre would diffuse out only half as fast as a gas weighing 1 gm per litre under otherwise identical conditions.

i.e. Rate of diffusion $\propto \dfrac{1}{\sqrt{\text{density}}}$

The above law of Graham is extremely useful in comparing the molecular weights of two gases, for molecular weight can be easily shown either from Avogadro's law or from perfect gas equation (3-II) to be proportional to density.

Therefore, $\dfrac{\text{Rate of diffusion of a gas, A}}{\text{Rate of diffusion of a gas, B}} = \sqrt{\dfrac{\text{mol. wt. of B}}{\text{mol. wt. of A}}}$

Thus, the relative rate of diffusion of methane and CO_2 would be $1/\sqrt{16} : 1/\sqrt{44}$ *i.e.* $5:3$ approximately, and hydrogen is the most diffusible of all gases. This property that gases of different molecular weights diffuse out at different rates can be employed for the separation of the constituents of a gaseous mixture and such a process of separation or concentration of the constituents of a gaseous mixture based on the diffusive properties of gases is called *atmolysis*.

Experimental determination of the rate of diffusion being rather difficult, it is customary to compare the rates of *effusion*

of two gases through a small aperture under the same average pressure. The difference between diffusion and effusion is that in the latter case, the gas is forced out through a small opening of the pinhole type by some external pressure, while in the case of diffusion, the gas automatically comes out of a porous partition due to the chaotic movement of its molecules. But the two processes are essentially the same and are governed by the same law of Graham. Effusion experiments are particularly suitable for molecular weight determination because it is equally applicable to a *mixture* or to a pure compound.

If the time required to effuse out for equal volumes of two gases are t_a and t_b respectively, then since the time of effusion *is inversely proportional to the rate*, we have

$$\frac{t_a}{t_b} = \frac{\text{Rate of effusion of B}}{\text{Rate of effusion of A}} = \sqrt{\frac{\text{mol. wt. of A}}{\text{mol. wt. of B}}}$$

The proof of Graham's law on the basis of kinetic theory has already been given. The method of calculation of molecular weight by diffusion experiments is illustrated by the following simple example.

EXAMPLE. 2. It is observed that 100 c.c. of pure ozone effuse through a pinhole in a thin plate in 1 min. while under the same conditions 100 c.c. chlorine gas escapes in 72 secs. The vapour density of chlorine is 35·5. Find the molecular formula of ozone. [O = 16, Cl = 35·5]

$$\frac{\text{Rate of effusion for chlorine}}{\text{Rate of effusion for ozone}} = \frac{\sqrt{\text{density of ozone}}}{\sqrt{\text{density of chlorine}}}$$

$$= \frac{\sqrt{\text{mol. wt. of ozone}}}{\sqrt{\text{mol. wt. of chlorine}}} \quad \text{or} \quad \frac{60}{72} = \frac{\sqrt{\text{mol. wt. of ozone}}}{\sqrt{(2 \times 35·5)}}$$

or, approx. mol. wt. of ozone = 49·3.

Since ozone is a condensed form of oxygen, its molecular weight must be an exact multiple of 16. Therefore the exact molecular weight of ozone 48·0. Hence, the molecular formula for ozone is O_3.

Avogadro Number (N)—The number of molecules present in one gram molecule of any gas is the same, and this number is called Avogadro Number. This is a very important constant and has been determined recently by various different methods. The most reliable value so far obtained for this number is 6 × 10²³. The student should do well to memorize this value N. It is evident that the absolute weight of an atom in grams just 1/N times its atomic weight and similarly, for the weight of a molecule. This constant per c.c. for a gas at N.T.P. is sometimes called Loschmidt number.

The Avogadro number is so large that we can scarcely form any idea about it : this idea can be put forward in this way, that if we take a mol of any substance, say 2 gms of hydrogen and magnify each molecule as a tennis ball and put them together in a heap, the heap will grow as large as ten of our earth together. The vastness of the number of molecules in a gas at ordinary pressure is easily realised if it is remembered that even in the best vacuum ever produced, one cubic centimeter contains more molecules than the total human population of our globe.

SPECIFIC HEATS OF GASES

Definitions of C_p and C_v—When a gas is heated the amount of heat required to raise its temperature through 1°C depends upon the external conditions and is different if the heating is conducted at a constant pressure from what would be required if the heating is conducted at a constant volume. So, there are two well-defined specific heats for gases (i) Specific heat at constant volume denoted by c_v, and (ii) Specific heat at constant pressure denoted by c_p.

(a) *Specific heat at constant volume* (c_v) is defined as the quantity of heat required to change the temperature of one gram of a gas through 1°C, if during the heating, the volume of the gas is not allowed to change.

(b) *Specific heat at constant pressure* (c_p) is defined as the quantity of heat required to change the temperature of one gram of a gas through 1°C the pressure upon the gas being maintained constant throughout the heating (of course, the volume will change in this case).

Chemists generally deal with mols, and so molar heat capacity *i.e.* molar heat, would enter more into our discussion. Molar heat is the specific heat multiplied by the molecular weight and is denoted by $C_v = M.c_v$ and $C_p = Mc_p$. Some typical values are shown in the table to follow. It is remarkable that though mercury and helium differ so widely in their physical and chemical nature they have practically the same specific heat. This is easily explained as shown below on the basis of kinetic theory.

Specific Heat and Kinetic Theory—If a gas is heated at, say, constant volume, the supplied heat goes (a) to increase the kinetic energy of the gas molecules, and (b) to increase the intra-molecular energy (*i.e.* energy inside the molecule, which may be vibrational, rotational, etc.). Therefore,

C_v = Increase in total kinetic energy for 1°C + Increase in intra-molecular energy.

But according to the kinetic theory of gases, for 1 mol. of a gas, $PV = \frac{2}{3}$ kinetic energy.

$$\text{or, Kinetic energy} = \tfrac{3}{2}PV = \tfrac{3}{2}RT$$
$$= \tfrac{3}{2}R \text{ (for 1°C rise in temperature)}$$

Therefore, $C_v = \tfrac{3}{2}R + a$,

where 'a' is the *intra-molecular energy*, expressed in thermal units. Since the value of R in thermal units is about 2 calories, C_v of an ideal gas should be greater than three.

If the heating is conducted at constant pressure, the gas during heating expands and therefore the heat supplied goes (a) to increase the kinetic energy of the molecules; (b) to supply the internal energy of the molecules and (c) to do external work.

Therefore, C_p = Increase of molar kinetic energy per degree + Intramolecular energy per degree + External work.

If during the heating, the gas expands from a volume V_1 to a volume V_2, at a constant pressure P, then the external work
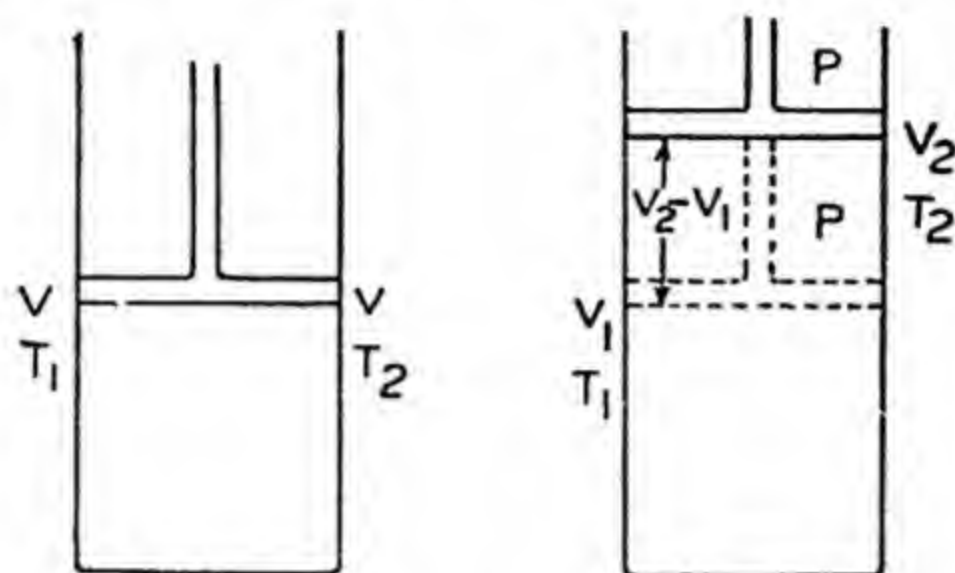
Fig. 7—Heating a gas at constant
volume and at constant pressure.

done by the gas is the product of the pressure and the change of volume. This is shown diagramatically in Fig. 7.

$$\therefore \quad \text{External work} \atop \text{per gm. mol} \Bigg\} = P(V_2 - V_1) = PV_2 - PV_1$$

$$= RT_2 - RT_1 = R(T_2 - T_1)$$
$$= R \text{ (if the temperature is increased}$$
$$\text{through } 1°C \text{ only).}$$

$$\therefore \quad C_p = \tfrac{3}{2}R + a + R$$
$$C_p = \tfrac{5}{2}R + a$$

where 'a' has the same significance as before.

(a) **Difference between the two Molar Specific Heats—** For any gas, the difference between the two specific heats is therefore,

$$C_p - C_v = (\tfrac{5}{2}R + a) - (\tfrac{3}{2}R + a)$$
$$= R = 2 \text{ cals [Since, } R = 2 \text{ cals approx.].}$$

The table to follow illustrates the truth of this relation. The significance of the observation that $C_p - C_v$ is a constant is that the work done in expansion against the atmosphere is independent of the gas doing the work.

(b) **Ratio of the two Specific Heats—** The ratio of the two specific heats is usually denoted by γ and is, therefore, given by (taking R = 2 approx.),

$$\gamma = \frac{C_p}{C_v} = \frac{\tfrac{5}{2}R + a}{\tfrac{3}{2}R + a} = \frac{5 + a}{3 + a} < 1.66 > 1$$

The value of the above fraction always lies between 1 and 1·66 (= 5/3), *and therefore* γ *the ratio of the two specific heats is a fraction which always lies between 1 and 1·66.* The following

table of specific heats for different gases brings out the truth of the above statement.

If a gas is *monatomic* there can be no energy within the molecule due to the vibration of the component atoms and ordinarily there is no rotational contribution to the energy *i.e.* for such a gas, $a=0$; therefore, for a monatomic gas $\gamma=\frac{5}{8}=1\cdot66$. This relation has been used to decide the monatomic nature of the inert gases and mercury as shown in the table.

N.B.—It remains to be pointed out that in the relation, $C_p-C_v=R$. C_p and C_v are molar heats whereas in $\gamma=C_p/C_v$, the C_p and C_v terms are either molar heats or specific heats for they are expressed in terms of a ratio.

MOLAR HEATS OF GASES

Gas	C_p	C_v	$C_p/C_v=\gamma$	Mol. Complexity
Helium	5·0	3·0	1·66	Monatomic
Mercury vapour	5·0	3·0	1·66	Monatomic
Hydrogen	6·88	4·88	1·41	Di-atomic
Oxygen	6·96	4·96	1·40	Di-atomic
Carbon dioxide	9·55	7·55	1·30	Tri-atomic
Water vapour	8·65	6·65	1·28	Tri-atomic
Ether vapour	27·8	25·8	1·08	Fifteen atomic

Experimental Determination of $\gamma=C_p/C_v$ of a Gas— The simplest and most widely used method is due to Kundt, which depends in principle on the determination of the velocity of sound, v, in a gas of pressure, P and density, d, given by the expression,

$$v=\sqrt{\gamma P/d}$$

and so knowing v, γ can be calculated.
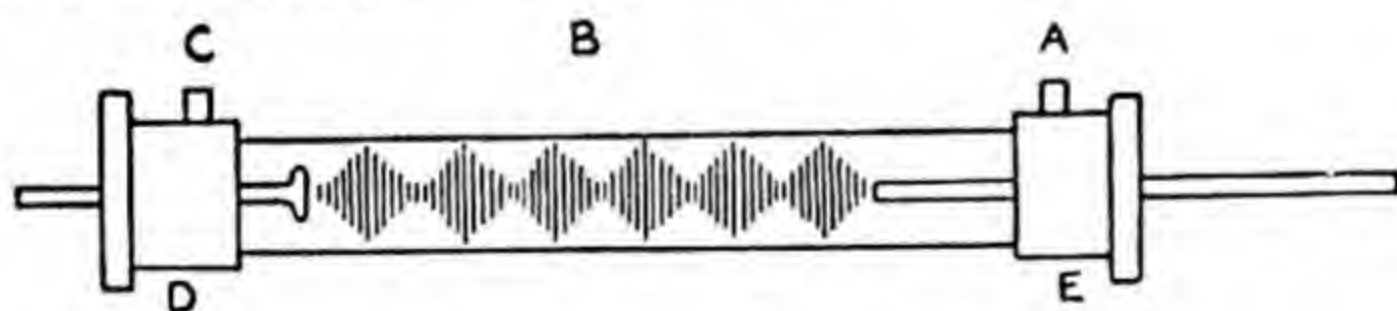
Fig. 8—Determination of γ: Kundt's tube

Kundt's apparatus consists of a glass tube, B (Fig. 8) a meter or more in length which contains a small amount of a light powder, such as lycopodium or saw-dust. The tube is closed at both ends by rigid stoppers. Through one stopper C passes a glass or metal rod terminating at a flat end, while a longer similar rod passes through the other stopper, A. The latter rod is firmly fitted at its centre by the stopper. The tube is filled with the gas and by striking the second rod with a cloth coated

with rosin powder, a harsh sound is produced and the rod is set into vibration which in turn sets the gas inside also into vibration. The powder inside arranges into striated heaps as a standing wave is produced inside. The first rod is slightly pushed or pulled out to get the best results. The distance between two neighbouring heaps is measured and is, of course, equal to half the wavelength, λ.

The tube is now filled with air at the same pressure and the experiment repeated. Now we should have

$$\frac{\lambda_1}{\lambda_2} = \sqrt{\frac{\gamma_1 d_2}{\gamma_2 d_1}}$$

and so knowing γ and d for air, γ for the gas is easily obtained.

EXAMPLES WORKED OUT—In working out problems the equation $PV = nRT = (g/M)$ RT is of paramount importance. It is to be carefully borne in mind that R should be expressed in the same system of unit as P and V and in this book R will be expressed as 0.082 *litre atmosphere/degree*.

EXAMPLE 3. *What is the volume occupied by 5 gms of benzene vapour at 200°C and 750 m.m. pressure?*

$P = 750$ m.m. $= \frac{750}{760}$ atmos.

$g = 5$ gms
$M = C_6H_6 = 78$
$R = 0.082$ litre-atmos/degree

$T = 273 + 200 = 473°$ abs.

Using these values in the equation, $PV = (g/M)$ RT, we have

$$\frac{750}{760} \times V = \frac{5}{78} \times 0.082 \times 473$$

or $V = \dfrac{5 \times 0.082 \times 473 \times 760}{750 \times 78}$

$= 2.52$ litres.

EXAMPLE 4. *34.23 cc. of phosphine gas at 20°C and 70 cm. weighs 0.0447 gms. What is its molecular weight?*

$P = 70$ cm. $= \frac{70}{76}$ atm.

$V = 0.03423$ litres
$g = 0.0447$ gms
$R = 0.082$
$T = 293°$ abs.

Substituting these values,

$$\frac{70}{76} \, 0.03423 = \frac{0.0447}{M} \times 0.082 \times 293$$

$\therefore$ Mol. wt. $M = \dfrac{0.0447 \times .082 \times 293 \times 76}{70 \times .03423}$

$= 34.1$.

EXAMPLE 5. *The vapour of a hydrocarbon is 2.7 times heavier than oxygen. What is its molecular weight? Calculate its exact molecular weight given that it contains 92.25 per cent carbon (C—12.00, H—1.0078).*

$M = \dfrac{gRT}{PV} = d \, \dfrac{RT}{P}$. For two gases, $\dfrac{M_1}{M_2} = \dfrac{d_1}{d_2}$.

Therefore $M_1 = M_2$, $d_1/d_2 = 32 \times 2.47 = 79.04$.
Now, wt. per cent $C = 92.25$; wt. per cent $H = 7.75$
$\therefore$ atomic ratio of $C = 92.25/12 = 7.60$.
and atomic ratio of $H = 7.75/1.0078 = 7.69$.
$\therefore$ the empirical formula is $(CH)x$

Since, $(CH)x$ has mol. wt. approx. 79.04, x is evidently 6. Therefore, the formula for the hydrocarbon is C_6H_6 and exact molecular weight is $6 \times (12.00 + 1.0078) = 78.047$.

EXAMPLE 6. *A litre of air weighs 1.293 gms., at N.T.P. At what temperature will a litre of air weigh 1 gm., the pressure being 72 cm?*

At N.T.P. $P = 1$ atoms : $V = 1$ litre ; $g = 1.293$: $T = 273$

At the reqd. temp. T_1, $P_1 = 72/76$ atoms : $V_1 = 1$ litre. $g_1 = 1$ gm.

Now $PV = (g/M) RT$ and $P_2 V_1 = (g_1/M_1 RT_1$.

$$\frac{PV}{P_1 V_1} = \frac{g}{g_1} \cdot \frac{T}{T_1} \qquad \text{or } T_1 = \frac{g.P_1.V_1.T_1.}{g_1.P.V.}$$

$$= 334 \cdot 4° \text{ Abs.} = 61 \cdot 3°C.$$

EXERCISES

(a) Ideal Gas Equation

1. What is the exact experimental implication of the statement, "all gases are ideal at sufficiently low pressure".

2. Deduce the value of the molar gas constant, R, in any three systems of units. What will be its value if meter, kilogram and hour are taken as the fundamental units. [$1 \cdot 077 \times 10^5$]

3. Write short notes on :—Isothermals, isobars, and dimensions of R and RT.

4. What form does Boyle's law take if an ideal gas is placed in a gravitational field? In what sense is the law true now?

5. Criticise and correct the statement, "All ideal gases expand equally for equal rise of temperature independent of their mass or chemical nature".

6. Is the following a correct alternative statement of Charles' law : The rate of expansion per degree at constant pressure for one mol of any ideal gas is the same independent of its chemical nature or its temperature. Discuss critically showing its compatibility or otherwise with Charles' law.

Can you restate Charles' law (both forms as given in the text) by using density in place of volume.

7. Through an absorption bulb containing acetone thirty litres of air are slowly bubbled at 30°C and atmospheric pressure, and the bulb is found to lose 25 grams of acetone. Calculate the saturation pressure of acetone. [$265 \cdot 8$ mm.]

8. What is the volume of $2 \cdot 5$ gms. of ether at 40°C and 720 mm. pressure? Calculate the absolute density and density referred to oxygen under the same conditions. [$914 \cdot 6$ c.c. ; $\cdot 00273$ gms/c.c. ; $2 \cdot 31$]

9. Calculate the density at N.T.P. of N_2, H_2, CO_2, sulphur hexafluoride and uranium hexafluoride (U—238, F—19).

[$\rho N_2 = 0 \cdot 001246$, $\rho H_2 = 0 \cdot 000089$, $\rho CO_2 = 0 \cdot 001958$, $\rho SF_6 = 0 \cdot 006497$.
$\rho UF_6 = 0 \cdot 015664$ g./c.c.]

10. Three litres of chlorine measured at 0°C and 760 mm pressure weigh $9 \cdot 621$ gms. Calculate the molecular weight of chlorine. [$71 \cdot 8$]

11. The density of a gas is $0 \cdot 20$ referred to mercury vapour (monatomic). What is the molecular weight? [40]

12. How many grams of hydrogen will be required to fill a 10 litre vessel at −30°C and 300 mm pressure. [$0 \cdot 396$ gm.]

13. 20 gms. of solid iodine, I_2, are placed in a flask of 1 litre capacity and the flask is then filled with nitrogen at 20°C and 750 mm and sealed. The flask is then heated to 100°C at which temperature all of the iodine is vaporised. What pressure will be developed? The density of solid iodine is $4 \cdot 55$ gms. per c.c. I = 127 and is a diatomic gas. [$PI_2 - 2 \cdot 41$; $PN_2 - 1 \cdot 25$; Total − $3 \cdot 66$ atmos.]

14. A bottle is heated with its mouth open from 15° to 100°C. What fraction of the air originally contained in the vessel is expelled? [$29 \cdot 5\%$]

15. Calculate the number of molecules per c.c. at 30°C in an extremely high vacuum produced by mercury diffusion pump, viz., $10-^7$ mm of mercury.
[$3\cdot19\times10^9$]

16. Suppose the inhaled air has an aqueous tension of 5 m.m. and the exhaled air is nearly saturated at body temperature, 38°C, with water vapour, calculate the weight of water lost by a person in the course of a day in this manner, assuming that the normal man breaths 10,000 litres per day. Sat. Press. of water at 38°C = 49·7 mm. [414·6 gms.]

17. In an adsorption experiment, 5 gms. of charcoal (apparent volume is 8·3 c.c.) when introduced in a closed space of volume 80 c.c. containing argon at 720 mm pressure at —50°C. the pressure fell to 49·7 m.m. Calculate the amount of argon adsorbed per gm. of charcoal in the above experiment. [0·0276 gm.]

(b) Kinetic Theory.

18. State the fundamental assumption of the kinetic theory of gases. Show how the theory supports (a) Avogadro's Law and (b) Graham's Law of diffusion.

19. On the basis of Kinetic theory, deduce (a) Boyle's Law, (b) Charles' Law.

20. Write short notes on :—Avogadro number, mean free path. r.m.s. speed, atmolysis, and kinetic energy per molecule per degree of freedom.

21. Calculate the average speed of a molecule of (a) hydrogen at 0°C and (b) carbon dioxide at 100°C. [184,500 cm./sec. ; 45,980 cm/sec.]

22. Calculate the average kinetic energy of a molecule of carbon dioxide at 15°C. What is its velocity?
[$5\cdot96\times10^{-14}$ erg : 403·7 metres per sec.]

23. Calculate the average kinetic energy of a nitrogen molecule at 50°C. How fast would an one gram weight have to move in order to have the same kinetic energy?
[$6\cdot69\times10^{-11}$ erg : 11·5 cm. per year.]

24. At what temperature is the r.m.s. speed of a hydrogen molecule 1·2 miles per second?
[299·1°K]

25. A box is divided by a thin partition into two equal compartments. and they are filled with an equal number of hydrogen and heavy hydrogen molecules respectively. If the pressure in the hydrogen compartment is one cm. what is the pressure in the other compartment? [1 cm : 1 cm.]

What will be the pressure if the partition be removed?

26. A long rectangular box is filed with chlorine (at. wt. —35.45) which is known to contain only $^{35}Cl_2$ and $^{37}Cl_2$. If the box could be divided by a partition and the two types of chlorine molecules put in the two compartments respectively, calculate where should the partition be if the pressures on both sides are equal. Is this pressure the same as the original pressure? How are the density and the number of molecules per c.c. in the two compartments related to the respective original values.

27. Supposing one molecule in a gas is somehow visible. What will be observed with regard to its path of flight and velocity with passage of time.

Ladenburg found that a sample of ozonised oxygen containing 86·16% of ozone by weight required 430 seconds to diffuse under conditions where pure oxygen required 367·5 seconds. Determine the vapour density of ozone.
[22·9]

28. State Graham's law of diffusion, and show how it can be deduced from the kinetic theory of gases.

29. A 4 to 1 mixture by volume of helium and argon is allowed to diffuse through capillary tubes into an evacuated space. What is the

composition of the gas which first passes through?   [He : A : : 12·64 :1]

30. In the preceding question, what effect would a variation in temperature or pressure have on the composition of the gas emerging into the evacuated space?

31. The four tyres of a motor car are respectively filled with helium, hydrogen, air and nitrogen. In what order will these tyres require to be reinflated?

32. 75 c.c. of a gas were collected over mercury in a tube closed at the top by a plaster of Paris plug (porous). On standing in air for some time, and when the mercury level becomes constant again, the volume was found to be 123 c.c. What is the molecular weight of the gas? (1 litre of air weighs 1·293 gms. at N.T.P.).   [78]

33. What is the ratio of the rates of diffusion of vapours of H_2O and heavy water, D_2O. If a sample of vapour contains equal number of molecules of water (H_2O) and heavy water, what will be relative proportion in the first fraction which would diffuse out.   [1·05 :1]

34. How would you proceed to ascertain whether a given gas is monatomic or diatomic? Discuss the principle underlying the method used. How has the monatomic nature of Argon been established?

35. What do you understand by specific heat at constant volume and at constant pressure for a gas? How would you prove that the ratio of the two specific heats for a monatomic gas is equal to 1·66 and that for other gases it is less than 1·66 but greater than 1.

The specific heat for a gas at constant volume is C·075 and that at constant pressure is 0·125. Calculate the molecular weight of the gas. [40]

36. Can you suggest a kinetic theory interpretation of the common saying that wet cold weather is much more penetrating than dry cold weather?

CHAPTER III

REAL GASES

Deviations from Ideal Behaviour— It has been already pointed out (P. 7) that actual gases follow the ideal gas equation to a fair degree of approximation under ordinary conditions. But under high pressure or at sufficiently low temperature, the ideal gas equation is not even approximately followed, and wide departure from this 'norm' is observed. The departure at *high pressure* is such that the actual gases are *less compressible* (*i.e.*, have larger volume) than what is expected from the ideal gas equation. On the other hand the deviation due to *low temperature* acts in the sense of making the actual gas *more compressible* than the ideal gas. We owe to the careful experiments of Regnault, Andrews (1869), Amagat (1880) and others, the knowledge about the behaviour of real gases under a wide range of variation of temperature and pressure, which will be discussed below.
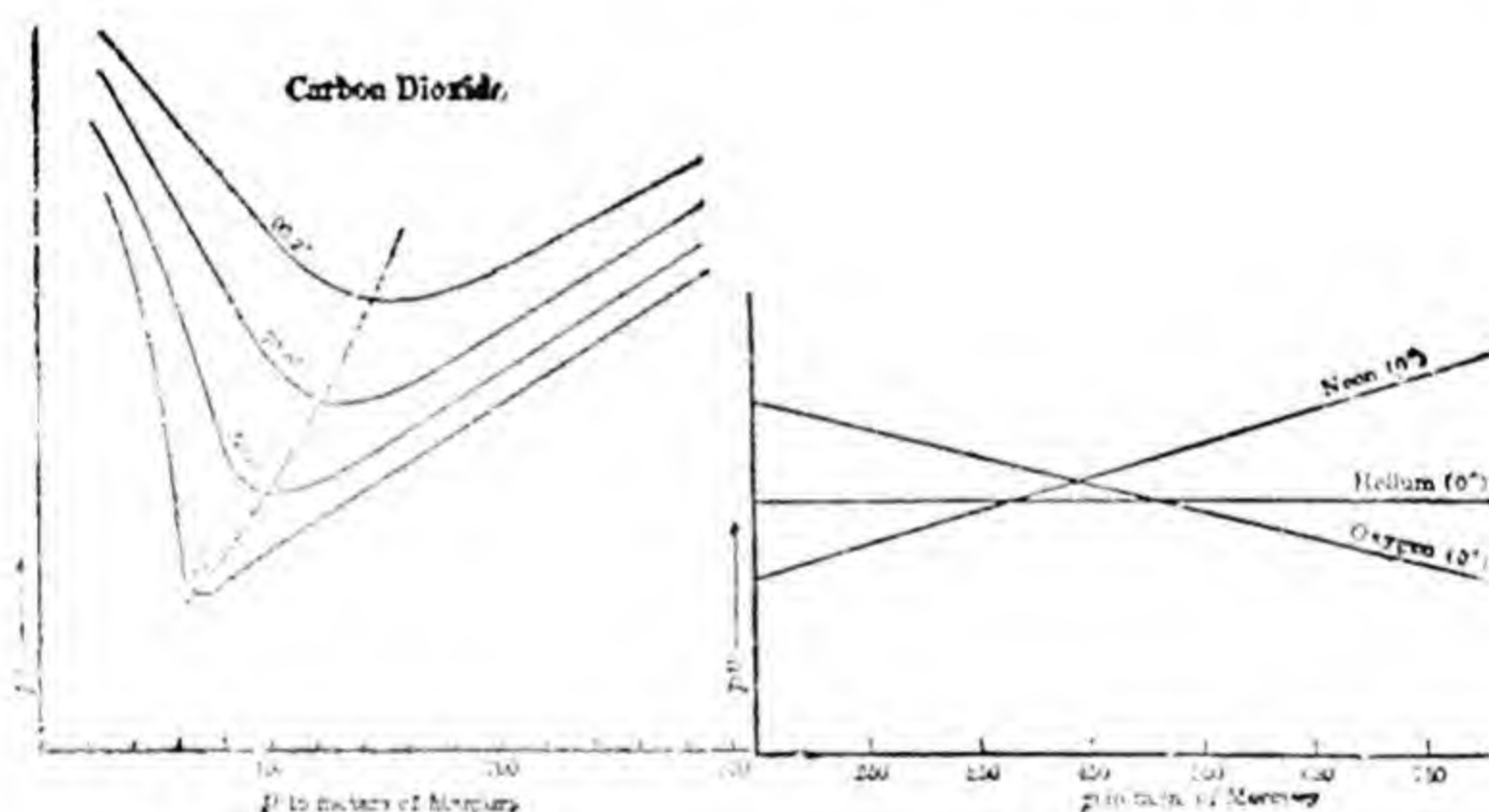
Figs. 9 & 10.—Amagat's curves for some common gases (PV in arbitrary and different units).

Amagat's Curves—In order that the departure of any actual gas from ideal behaviour, be known immediately from the graph, Amagat plotted PV against P at a constant temperature. These curves are known as Amagat's curves. If the gas be ideal, the Amagat curve will be a straight line parallel to the pressure axis with a constant ordinate equal to RT. A less compressible gas will be above this line and a more compressible gas will be below this line.

Some typical Amagat's curves are shown in Figs. 9 and 10. In the case of CO_2, N_2 etc., PV gradually decreases, attains a minimum and then continually increases with pressure; while in others, the product PV continually increases with pressure,

showing that at a higher pressure the compressibility is less than that expected from Boyle's law. It will be also noticed from the graphs for CO_2 that the region of higher compressibility increases with lowering of temperature. The above behaviour is the general trend which can be summed up by saying that *a gas is the more compressible the lower the temperature* and is *the less compressible the higher the pressure* (Fig. 11 & 12). Helium at 0°C under not too high pressure is perhaps under just the right condition for ideal behaviour as will be apparent from Fig. 10 where the curve for helium runs almost parallel to the pressure axis.

Compressibility Factor— This departure of actual gases from ideal behaviour is very often expressed nowadays by compressibility factor, symbolised by z (or κ) and defined by the equation,

$$PV = znRT, \text{ or } z = PV/nRT$$
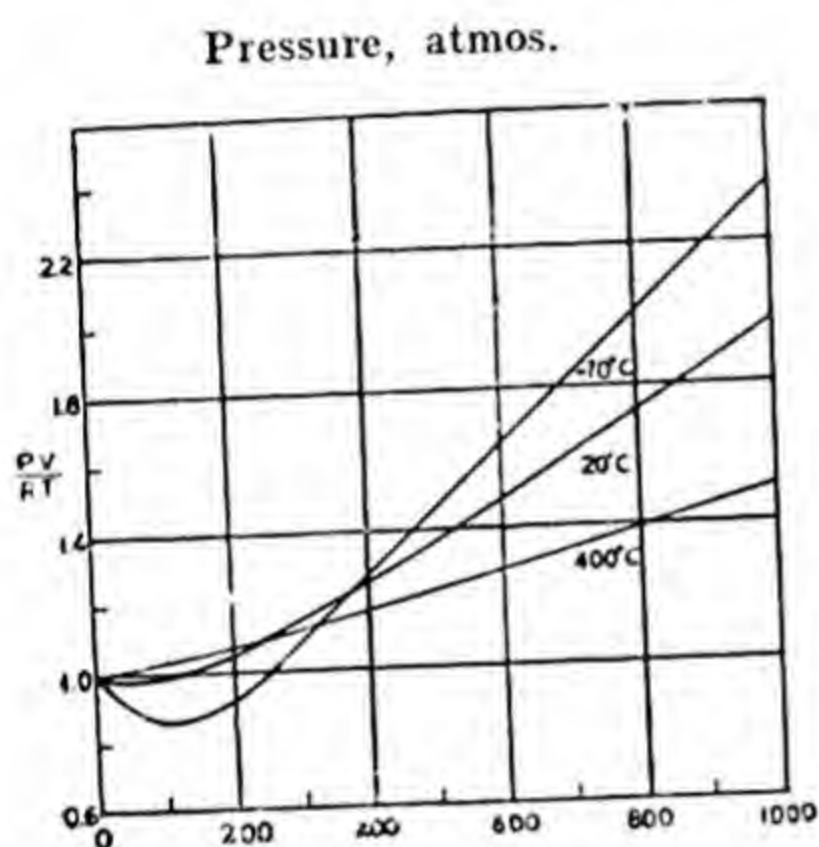
Fig. 11—Compressibility factor curves for N_2
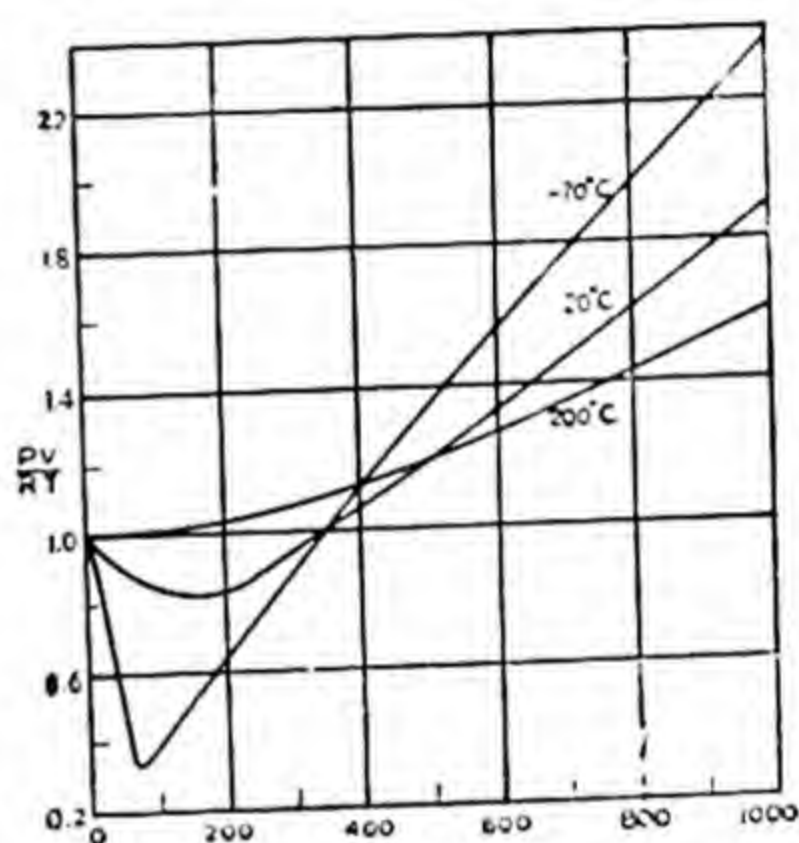
Fig. 12—Compressibility factor curves for ethylene

For a perfect gas, $PV = nRT$, and hence z has a value of unity and for any actual gas the departure of z from unity shows the extent of its deviation from ideal behaviour. It will be noted from the above equation that at any temperature the compressibility factor z is the ratio of the actual volume of the gas to the ideal volume. Hence, a value of z greater than unity means that it is less compressible, and a value less than unity means that it is more compressible than that demanded by the perfect gas equation.

The variation of compressibility factor over a wide range of pressure is shown for methane and nitrogen in Figs. 11 and 12 respectively. These two diagrams clearly show the trend of deviation caused by temperature and pressure change as discussed in the previous section. It is noteworthy that in the one thousand atmosphere ranges the ideal gas equation is often more than one hundred per cent in error. Of course, at sufficiently low

pressure all the curves attain the perfect gas value unity for z, *i.e.*
PV per mol equals RT.

It is customary to plot z against the reduced pressure P/Pc
at a given reduced temperature T/Tc. The subscript c standing
for critical values. Since all gases show approximately the same
behaviour when expressed in this way, a single graph serves to
represent the behaviour of all gases. Such compressibility factor
graphs generally have more or less the appearance of Amagat's
curves.

Van der Waals Equation—Attempts were naturally made
to offer an explanation based on the molecular kinetic theory
as to why the real gases fail to conform to the ideal gas equation.
Of these attempts the simplest and the most successful is that
due to the Dutch chemist, van der Waals (1873). According to
van der Waals the reasons for the failure of the ideal gas equation,
PV = RT over an extensive range of temperature and pressures,
are two-fold.

(*a*) Firstly, in our kinetic deduction we have assumed that
the volume which is accessible to a molecule for free movement,
is the total volume of the containing vessel. But, since the
molecules themselves are incompressible and have a volume of
their own, which may not be a negligible fraction of the total
volume of the gas at high pressures, the free space inside the
vessel is not V but is less than V, say, $(V - b)$ where b is a correc-
tion term representing the excluded volume and this $(V - b)$ varies
with pressure according to Boyle's law.

(*b*) Secondly, in our kinetic deduction we have neglected
the intermolecular attraction, but in real gases there exists an
attraction operating between two molecules as is proved by the
existence of Joule-Thomson effect. This attraction depends,
besides other factors, on the distance between them and their
masses. For a molecule at the centre this force is nil being
balanced by attractions from all sides but as the boundary is
approached these forces increase and act towards the centre from
all sides. The net effect is that the real pressure acting on the
gas is not only the external pressure P, but also this additional
pressure acting in the same direction as the external pressure.

If we imagine in a gas two layers of molecules, each layer
will attract the other with a force proportional to their number,
i.e. proportional to the density. Therefore, the total force will
be proportional to the density of each layer and so will be pro-
portional to the square of the density of the gas, *i.e.* inversely
proportional to square of the volume, which van der Waals puts
as a/V^2 ($a=$const.). Therefore, the net effect is that, as if the
gas is acted upon by an increased pressure $P + \dfrac{a}{V^2}$ instead of P.

So the gas equation becomes

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

which is the well-known equation given by van der Waals in the year 1873. This pioneering attempt by van der Waals to interpret real gases was so timely and illuminating that Boltzmann hailed van der Waals as the Newton of real gases.

The two corrections introduced by van der Waals act in opposite directions, the *volume correction 'b'* increasing the value of PV and the *attraction correction* a/V^2 decreasing the value of PV from what is to be expected from ideal gas laws. At low pressure the attraction correction more than balances the volume correction, but at high pressure the volume correction predominates. So, if a gas initially at low pressure be subjected to a gradual increase of pressure the product PV will gradually decrease, reach a minimum and then continually increase with pressure. For many gases this variation is quite considerable, an idea of which can be obtained from the Amagat's curves (*vide* Fig. 10) as also from the following Table compiled from the data of Amagat for ethylene at 20°C. This table also demonstrates that though the value of PV varies over a wide range in utter disagreement with the perfect gas equation, the agreement with the van der Waals equation is quite remarkable. More remarkable however is the fact that this equation is not only applicable to gases but is equally applicable to gas-liquid transition and to liquids *i.e.* over the whole range of behaviour of fluids (*vide* Ch. V).

ETHYLENE AT 20°C

Pressure (atmos.)	PV (arbitrary units)	
	Observed by Amagat	Van der Waals Value
1·0	1000	1000
31·6	914	895
45·8	721	782
72·9	416	397
84·2	399	392
110·5	454	456
176·0	643	642
233·6	807	805
282·2	941	940
329·1	1067	1076
398·7	1248	1254

The values of the constants a and b for some gases are given in the following table (note the units of a and b). It should be noted that easily condensable gases like carbon tetrachloride and ethyl ether have comparatively higher values for a, which indicate strong intermolecular attraction. Also, b is a measure of the size of the molecules and is roughly four times the volume of the molecules considered as simple spheres.

Van der Waals Constants

Gas	a, Atmos $\times$ (c.c.)^2/mol^2	b, c.c./mol.
Hydrogen	0.10×10^6	23.0
Oxygen	1.36×10^6	31.6
Nitrogen	1.35×10^6	38.6
Ammonia	4.17×10^6	37.1
Ethylene	4.47×10^6	57.1
Chlorine	5.35×10^6	46.1
Water	5.46×10^6	30.5
Carbon tetrachloride	20.86×10^6	195.3
Ethyl ether	17.38×10^6	134.4

For applications of van der Waals equation to the pheno-
menon of condensation, *vide* Chapter V.

Other Equations of State— Many other equations of state,
both semi-theoretical and empirical have been proposed from
time to time to express the behaviour of actual gases with better
precision. The theoretical foundation of none of them seems
to be any better than that of van der Waals and hence van
der Waals equation is still regarded the best for any theoretical
investigation. However, for some type of problems, van der Waals
equation is inconvenient and other equations are used. Some of
these equations which have attracted some attention are given
below.

(a) **Berthelot Equation**—

$$\left(P + \frac{A}{TV^2}\right)(V-B) = RT$$

i.e., an equation of van der Waals type where the constant a is
replaced by A/T. This equation of Berthelot, by an algebraic
manipulation similar to that used for obtaining the equation of
corresponding states in Ch. V, can be easily transformed to its
more familiar form,

$$PV = nRT\left[1 + \frac{9PT_c}{128P_cT}\left(1 - \frac{6T_c^2}{T^2}\right)\right]$$

where the subscript c indicates the corresponding critical
constants.

(b) **Dieterici Equation** (1899)—This equation in essence is
similar to that of van der Waals except that the pressure correc-
tion is done by introducing an exponential factor as shown below.

$$P(V-b)e^{\frac{A}{RTV}} = RT$$

(c) **Beattie-Bridgman Equation** (1927)—

$$V = \frac{RT}{P} + \frac{\beta}{RT} + \frac{\gamma P}{(RT)^2} + \frac{\delta P^2}{(RT)^3}$$

where V is the volume occupied by one mol of gas at temperature T and pressure P, and β, γ and δ are constants which are related among one another by five different constants and temperature. This semi-theoretical equation containing five constants gives very accurate results over a wide range of temperature and pressure, even near the critical point.

(d) **Virial Equation** (1901)—Since any variable quantity, y can always be expressed, irrespective of any theory, with more and more precision by an algebraic expression of the type, $y = A + Bx + Cx^2 + Dx^3 + \ldots\ldots$ by including more and more terms in higher powers of x, such an equation has been used by various investigators to express PV as a function of $1/V$, i.e.

$$PV = RT + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \ldots\ldots$$

where B, C, D, etc., are constants depending on temperature only, and are called second, third, fourth, etc. *virial co-efficients* of the gas. This equation is sometimes called Kammerling Onnes equation. Since the contributions from the square, cube, and other higher power terms are necessarily smaller than the first two terms, the equation reduces to PV=constant at the temperature for which $B=O$. This temperature for any gas is called the Boyle Temperature, because Boyles' law is applicable to the gas at this temperature over a fairly wide range of pressure.

EXAMPLE 1. *Calculate the pressure necessary to compress a mol of oxygen at N.T.P. to one tenth its volume at constant temperature using (i) perfect gas equation and (ii) van der Waals equation.*

$T = 273$, $V = 2.24$ litres, a & b given

(i) $P = \dfrac{RT}{V} = \dfrac{0.082 \times 273}{2.24} = 10$ atm.

(ii) $(P + \dfrac{1.36}{(2.24)^2}$ $(2.24 - 0.0316) = 0.082 \times 273$

or $P = \dfrac{0.082 \times 273}{2.21} - 0.27 = 9.8$ atm.

EXAMPLE 2. *Using the a and b values given in the table in the text, calculate according to van der Waals equation the volume occupied by (a) 1 mol. of ethylene and (b) 1 gm of ethylene at 10 atmospheres at 0°C and compare the values with those obtained from the ideal gas equation.*

P = 10 $b =$ ·0571
$a =$ 4·47 $R =$ 0·82
V = ?   T = 273

(a) from van der Waals equation, we have

$(10 + 4·47/V^2)$ $(V - ·0571) = ·082 \times 273$

or $V - ·0571 = 22·4/(10 + 4·47/V^2)$

Neglecting a/V^2, V comes out to be 2·30 litres approximately. Now by the method of successive approximations, we have V = 1·85 litres whereas by PV = RT, V = 2·24 litres.

(b) Since, under identical conditions, volume is proportional to the number of mols, we have, in extension of (a) V = 2090 (1/28) = 74·64 c.c. the ideal value being 2240/28 = 80 c.c. The result may, however, be

obtained directly from van der Waals equation for n mols of a gas (see Q. 6 in the next exercise).

EXERCISES

1. Does a real gas, at a very high pressure, occupy more volume or less than that by an ideal gas under identical conditions? Does temperature have any effect on the above?

2. Point out the lines of reasoning in which van der Waals equation has been deduced. What are the units of a and b in the above equation?

3. Two van der Waals' gases have the same b values but different a values. Which of these would occupy greater volume under identical conditions?

4. Two van der Waals' gases have the same value for a but differ in b. Which one would be more compressible?

5. Van der Waals equation is usually written for one mol of a gas. Write down the form it would take for n mols.

(Hint : Convert the only extensive property in the equation, e.g., V into per mole basis i.e. for V substitute V/n).

6. Calculate the pressure developed in a one litre vessel containing 10 gms. ammonia at $0°C$ using (a) van der Waals equation and (b) the ideal gas equation.   [12·02; 13·17 atoms]

7. Taking the diameter of an oxygen molecule to be 3·88A, calculate the actual volume of a mol of oxygen and compare it with the volume occupied by a mol of oxygen gas at N.T.P. [18·41 c.c.; 1 :1216].

8. Distinguish between compressibility and compressibility factor of a gas.

9. Clearly discuss the *experimental significance* of the statement that all real gases approach ideal behaviour at sufficiently low pressure and sufficiently high temperature.

10. In a closed space containing one mol of a van der Waals gas at constant temperature the pressure is observed to be P. If another mol of the same gas is introduced in the above space, will the new pressure be 2P. Discuss fully.

11. What will happen to volume under same conditions as in the previous example except that the system is under constant pressure conditions, the volume being allowed to change.

CHAPTER IV

MOLECULAR WEIGHTS OF GASES. DISSOCIATION

Density and Molecular Weights of Gases— The density of gases varies over quite an extensive range. Thus, among substances which are gaseous at ordinary temperature, the lightest hydrogen has a density of only 0·09 gms per litre, whereas at the other end of the scale is sulphur hexafluoride which is nearly seventy times heavier. At a slightly elevated temperature we meet even heavier gases, for example, uranium hexafluoride which is about 176 times heavier than hydrogen.

The most important property of gas density, d is that it is very simply related to the molecular weight by the following equation which is easily obtained from equation (4)-II (P. 8).

$$M = g\frac{RT}{PV} = d\frac{RT}{P} \quad \cdots \quad \cdots \quad \cdots \quad 1\text{-}(IV)$$

Hence, knowing the density of a gas under definite external conditions, its molecular weight is easily calculated.

Experimental Methods of Determining Density—Various methods for the determination of density are in use all of which aim at the same thing, that is, to know the weight of a certain volume of vapour under definite conditions of temperature and pressure. The more common methods are—(a) Hofmann's method, (b) Regnault's method, (c) Dumas' method and (d) Victor Meyer's method.

(a) **Hofmann's Method—** The principle of the method is to vaporise a known weight of a liquid in the Torricellian vacuum of a barometer at a suitable high temperature and to measure the volume and the pressure.

The arrangement of apparatus is shown in Fig. 13. It consists of a graduated *barometer tube* nearly a metre in length filled with mercury and inverted over a trough of mercury. The barometer tube is surrounded with a wider jacket through which the vapour of a liquid boiling in a flask A (Fig. 13) is passed to keep it at a temperature at which the experimental liquid may freely evaporate. A small bottle or a bulb drawn out into a fine capillary is filled with a known *weight* of the liquid and is introduced in the vacuous space above the
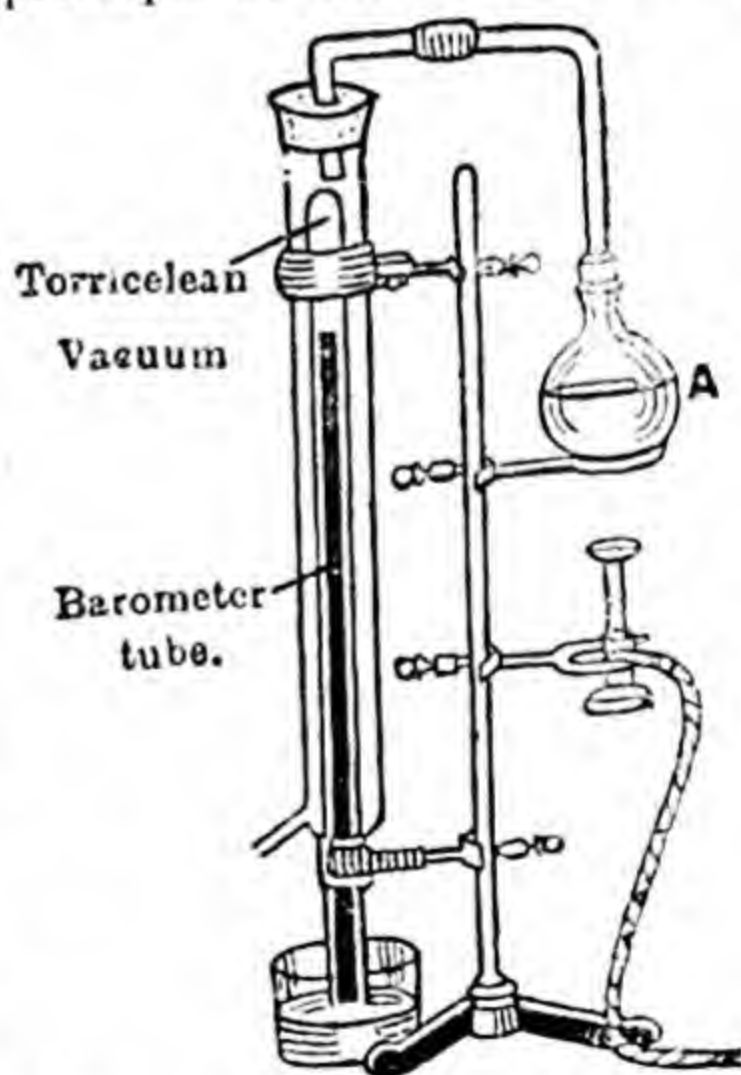
Torricelean Vacuum

Barometer tube.

Fig.—13. Hofmann's Apparatus.

3

mercury. The liquid at once evaporates and depresses down the mercury column. When the condition has become steady, the *temperature* is noted on a thermometer inside the vapour jacket (not shown in the fig.) and the *volume* is noted on the graduated tube. The *pressure* of the vapour is obtained by subtracting from the barometric pressure at the time of the experiment, the height of the mercury column in the tube. The volume occupied by a definite weight of the vapour at a known temperature and pressure being ascertained the vapour density and so, the molecular weight can be readily calculated.

This method is capable of giving good results, but the experiment is rather troublesome and cumbrous.

(*b*) **Regnault's Method**— The method of directly weighing a large volume of a gas is beset with difficulties due to the smallness of the weight of the gas compared with that of the containing vessel and due to the buoyancy of the displaced air, which latter should be accurately known. Regnault surmounted the difficulties in the following way. He counterpoised two thin metallic bulbs of equal capacity from the two arms of a balance, both the bulbs being evacuated. One of the bulbs was then filled with the gas under a known *pressure* and counterpoised against the vacuous bulb at the other arm, by adding known *weights*. The *temperature* during the experiment is kept constant and uniform. The *volume* of the bulb is next known by determining the weight of water which would completely fill the bulb at a known temperature. Thus, the weight of a known volume of gas at a definite temperature and pressure being known, the density and molecular weight of the gas can be easily calculated.

This method is very accurate and admits of application to permanent gases and substances which are gaseous at ordinary temperature over a wide range of pressures. Thus, it is suitable to be used for accurate molecular and atomic weight determination by the method of limiting density to be shortly described.

(*c*) **Dumas' Method**— The apparatus consists of a glass bulb with a drawn-out neck. The bulb is weighed dry and then filled with a few cc of the liquid. The bulb is heated in a constant temperature bath to a temperature at least 20°C above the boiling point of the liquid. A brisk stream of vapour issues out of the mouth, displacing all the air contained inside the bulb. When all the liquid is vaporised and the bulb is filled with the vapour of the liquid, the small opening is sealed with a blowpipe flame and the bulb after cooling is weighed. Both the atmospheric pressure and the temperature of the bath are noted. The bulb is then completely filled with water after breaking the end of the tube and weighed, from which the internal volume of the bulb is obtained. Thus the weight, volume, temperature and pressure of the gas are known and so, its density and molecular weight can be calculated.

This method is applicable only to liquids which can be easily vaporised and is available in a relatively large quantity. By using porcelain or metal bulbs, the method can be extended to the determination of the vapour density of such substances as zinc, cadmium, mercury, etc.

(*d*) **Victor Meyer's Method**—This method is widely used for the simplicity of the experimental procedure, but gives results of a lower order of accuracy. It differs from and is advantageous over all the foregoing methods in that here the vapour produced from a known weight of liquid is allowed to displace an equal volume of *air*, which is collected and measured at the room temperature and pressure.

A common form of the apparatus is shown in Fig. 14. It consists of a glass tube ending in an elongated *bulb* at the bottom and having a *sidetube*, which dips under water. The open end of the tube is closed with a rubber cork and a little sand or asbestos is placed at the bottom of the bulb to prevent cracking when the bulb containing the liquid is introduced. The glass tube is surrounded by an *outer jacket* of glass or copper in which is boiled a liquid having a boiling point considerably (*about 20°C*) higher than the substance to be vaporised. When the condition has become steady as indicated by

Gas burette

Detail of sample bulb

Vaporization tube in steam jacket

Fig. 14—Victor Meyer's Apparatus.

the cessation of escape of bubbles through the side-tube, a *graduated tube*, filled with water, is inverted over the end of the sidetube. The cork is now removed, and a sample bulb or a stoppered bottle (often called Hofmann's bottle) filled with a small amount (0·1–0·2 gm) of the liquid, is quickly introduced and the cork replaced. As soon as the bottle falls inside the vaporization tube, its stopper automatically opens out and rapid evaporation of the liquid takes place. The vapour thus produced expels an *equal volume of air* which comes out through the side-tube and is collected in the graduated tube at the room temperature at a pressure equal to that of the atmosphere diminished by the saturation tension of aqueous vapour. Thus, the volume of a known weight of vapour at a definite temperature and pressure being determined, the vapour density and molecular weight can be easily calculated.

EXAMPLES. VICTOR MEYER'S METHOD—The molecular weight can be calculated by three apparently different methods, from either of the following three relations:—(1) *The fundamental gas*
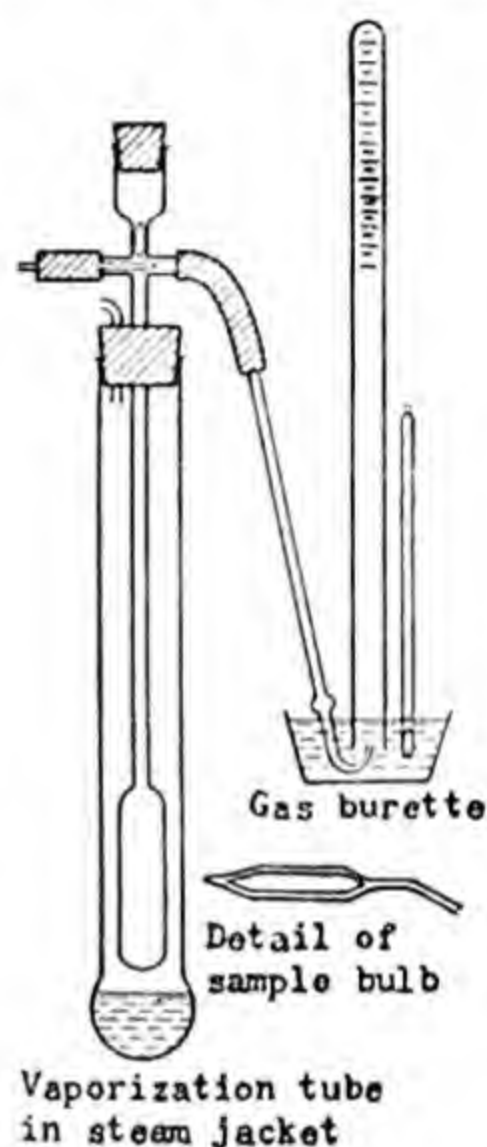
equation, $PV = nRT = (g/M) \times RT$, or (2) *Molar volume of any gas at N.T.P. is 22·4 litres*, or (3) *Molecular weight = 2 × vapour density*. The three methods of calculation are illustrated below, of which the student is recommended to use the first one whenever possible, as being the most direct and universally applicable.

The student should particularly note that all the three methods of calculation are in principle one and the same. For, each of them requires a constant derived from some other source. In the first method the value of R, in the second one, the constant 22·4 litres, and in the third method the absolute density of hydrogen are used and these constants can be shown to be simply related to each other.

EXAMPLE 1. *In Victor Meyer's Method, 0·1 gm. of a volatile liquid displaced 20 c.c. of air measured over water at 15°C and 765 mm pressure. Calculate the molecular weight of the liquid (vapour pressure of water at 15°C = 13 mm).*

(*a*) FIRST METHOD :—Pressure of the gas $= (765 - 13)mm. = \dfrac{752}{760}$ atm.

Volume of the gas = 20 c.c. = 0·02 litre.

Temperature $= (273 + 15)°$ abs. Mass of the gas = 0·1 gm.

R, the gas constant = 0·082 litre-atmosphere.
Substituting these values in the fundamental gas equation,

$$PV = nRT = \frac{g}{M} RT$$

We get $\dfrac{752}{760} \times \cdot 02 = \dfrac{0·1}{M} \times 0·082 \times 288$ or $M = 119·3$

(*b*) SECOND METHOD :—

Volume at N.T.P. = 18·76 c.c. $\left(\text{calculated from } \dfrac{PV}{T} = \dfrac{P'V'}{T'}\right)$

Now 18·76 c.c. are occupied by 0·1 gm.

∴ 22·4 litres are occupied by $\dfrac{0·1}{18·76} \times 22·4 = 119·4$ gms.

Since a gm. mol. of any gas occupies 22·4 litres, the molecular weight = 119·4.

(*c*) THIRD METHOD :—

Volume at N.T.P. = 18·76 c.c.; mass of the gas = 0·1 gm.

∴ the density $= \dfrac{0·1}{18·76}$ gms. per c.c

vapour density $= \dfrac{\text{density of gas}}{\text{density of hydrogen}} = \dfrac{0·1}{18·76 \times \cdot00009} = 59·2$

∴ molecular weight = 2 × vapour density = 2 × 59·2 = 118·4

This method is useful for calculating vapour density. A modification of this method would be to calculate density and therefrom to calculate M by using equation (1)—IV.

Method of Limiting Density—(*a*) *Molecular weight determination*. Though molecular weight is related to density by equation (4)-II (P. 8), the latter as shown below is necessarily only

$$M = \frac{dRT}{P} = \left(\frac{d}{P}\right)RT \qquad \dots \qquad \dots \qquad (1)\text{-IV}$$

approximate, because this equation is only another form of the ideal gas equation, which, we know, is only approximately obeyed by ordinary gases and vapours. We have however pointed out (P. 7) that all gases accurately obey the ideal gas equation at sufficiently low pressure and so the above equation would yield accurate values of M, provided the data for the above equation are obtained at vanishing pressures, *i.e.* at very low pressure,

$$M = \left(\frac{d}{P}\right)_0 RT \qquad \ldots \qquad \ldots \qquad \ldots \text{(2)-IV}$$

where the subscript zero indicates zero pressure. It is however, not experimentally feasible to carry out density measurements at very low pressures without an unduly large experimental error since the density becomes too small. The difficulty can be solved by having recourse to the method of graphical extrapolation to zero pressure.

This graphical extrapolation however, cannot be done by plotting density against pressure since the density of a gas vanishes at zero pressure. But the extrapolation may be easily accomplished by plotting the ratio of density to pressure (which has the physical significance of *density per unit pressure*) against pressure, and extrapolating this curve to zero pressure to obtain the value of (d/P) at zero pressure i.e. the ration $(d/P)_0$ of equation (2) above. This limiting ratio may be called density per unit pressure at zero pressure. This ratio does not become zero at zero pressure but tends to a limit. This may be easily grasped from the fact that when pressure decreases density also decreases, and in the limiting case of infinitesimally small pressure the density also becomes infinitesimally small and so their ratio always maintains a finite value.

DATA FOR LIMITING DENSITIES

Pressure atmos	Methyl Fluoride		Argon	
	wt. per litre	d/p	wt. per litre	d/p
1·0000	1·5454	1·5454	1·78364	1·78364
0·6667	1·0241	1·5361	1·18874	1·78311
0·3333	3·5091	1·5274	0·59419	1·78257

The method is illustrated from the above data for methyl fluoride. The values of d/p are plotted against pressure (Fig. 15) and the curve, which is almost a straight line, is produced (dotted portion in the fig.) to cut the axis of zero pressure (y-*axis*). The
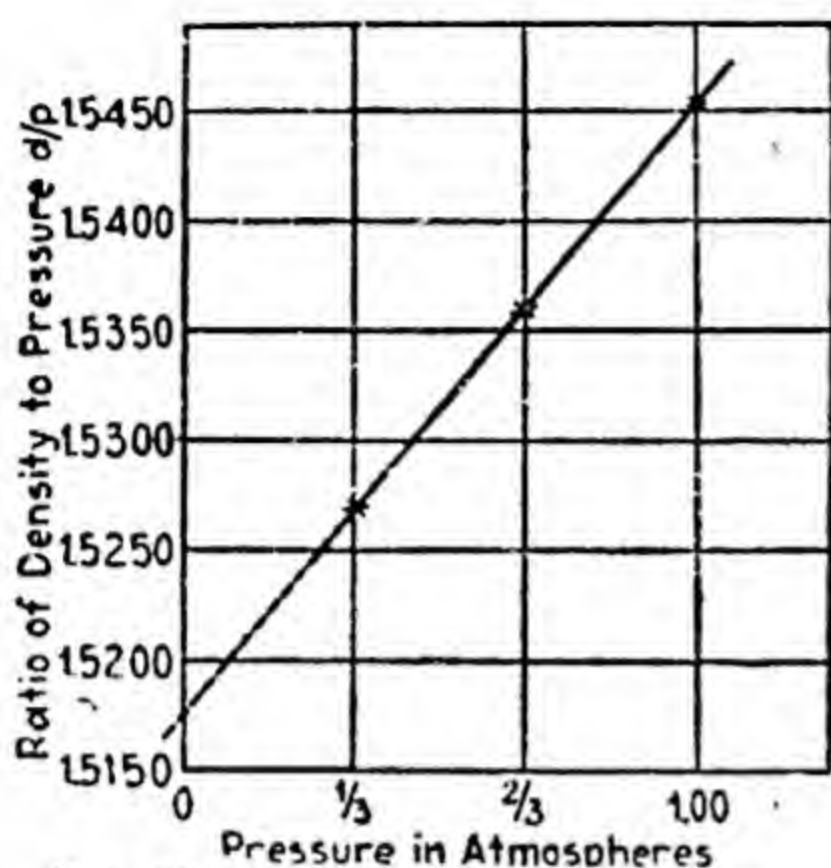
Fig. 15—Graphical Extrapolation
by the Limiting Density method.

ordinate of this point of intersection gives the value of limiting density *i.e.* the ratio of d/p at zero pressure when the behaviour of the gas becomes perfectly ideal. From the curve it is seen that the limiting value for d/p in this case is 1.5177. The corresponding value for oxygen is determined from a similar set of data and has been found to be 1.4277. Now, we have from eqn. (2), $1.5177 : 1.4277 = $ mol. wt. of $CH_3F : 32$ (mol. wt. of O_2), from which the molecular weight of methyl fluoride comes out to be 34.012.

Alternatively, we may use equation (2) directly. Knowing the limiting value of $(d/p)_0$ as above we may easily find the value of M by substituting in the above equation, which becomes exact under such limiting conditions.

(b) *Atomic Weight Determination*—This method can also be applied for accurate atomic weight determination. For, if it is an elementary gas like nitrogen, argon, etc., it is simply necessary to divide the molecular weight thus determined by the number of atoms per molecule. For example, for argon from the data in the foregoing table, the limiting value of d/p comes out to be 1.78204, corresponding to 39.235 as the molecular weight of argon. Since argon is monatomic this is also its atomic weight. Another procedure may be illustrated by calculating the atomic weight of fluorine. We have already found out that the molecular weight of methyl fluoride (CH_3F) is 34.012. From the known atomic weights of carbon (12.00) and hydrogen (1.008), the atomic weight of fluorine comes out to be $34.012 - (12.00 + 3 \times 1.008) = 18.99$, which compares very favourably with the value 19.00 obtained by chemical methods.

Abnormal Vapour Density—The experimental determination of vapour density has revealed some interesting facts. It has been found in some cases, for example, ammonium chloride, that the experimentally determined vapour density is much less than the theoretical value (*i.e.*, half the molecular weight). Thus Deville and Troost (1806) found that the vapour density of ammonium chloride at 350°C and 1040°C are 14.6 and 14.45 respectively, whereas the theoretical value should be 26.75. As our theoretical value is based on a relation, which is a simple corollary to the Avogadro hypothesis, either we have to limit the applicability of the Avogadro hypothesis, or we have to find

out some explanation for such deviations. Pebal showed that the very simple hypothesis of gaseous dissociation is sufficient to explain the anomaly. Under the experimental conditions, the molecules of ammonium chloride suffer dissociation to form ammonia and hydrochloric acid according to the equation, $NH_4Cl \rightleftharpoons NH_3 + HCl$, and so what we are measuring is the density of an equimolecular mixture of ammonia and hydrochloric acid together with some undissociated molecules of ammonium chloride. Since, due to dissociation the number of molecules increases, the volume of the system also increases and so, the density which is inversely proportional to the volume, decreases. If there is complete dissociation, the total number of molecules becomes doubled and so the density is halved which is approximately the case in practice.

Experimental Proof of Gaseous Dissociation—Such a bold assumption as above is based on firm experimental support. Firstly, it was shown by Than (1864) that when equimolecular quantities of ammonia and hydrochloric acid are mixed together at 350°C there is scarcely any contraction, conclusively proving that ammonia and hydrochloric acid molecules are capable of existing together at that temperature without combination to form ammonium chloride. The other evidence rests on a direct demonstration that ammonium chloride vapour contains ammonia and hydrochloric acid. The device used by Than and Pebal is shown in the diagram (Fig. 16).
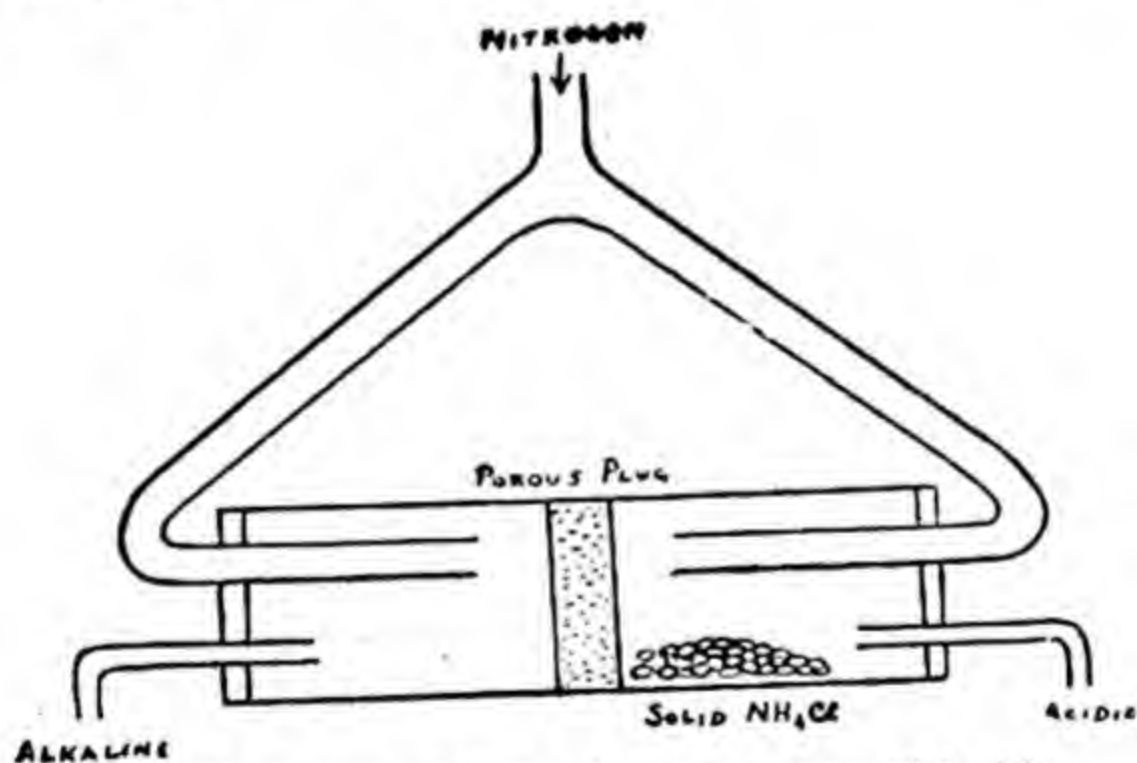
Fig. 16—Dissociation of Ammonium Chloride.

Some NH_4Cl is enclosed in a tube by the side of a porous plug made of compressed solid NH_4Cl. The tube is heated and a slow current of of an inert gas, say, nitrogen is passed on both sides of the porous plug. Now, ammonium chloride dissociates into ammonia and hydrochloric acid and the former being lighter diffuses more readily through the porous plug. So the gas which comes out from the other side is found to be alkaline due to an excess of ammonia, while the gas which issues out from the side of the ammonium chloride is found to be acidic due to an excess of hydrochloric acid. This experiment proves beyond doubt that ammonium chloride vapour is dissociated into ammonia and hydrochloric acid.

Further Examples of Gaseous Dissociation— The idea of gaseous dissociation which has been so successfully applied to explain the abnormal vapour density of ammonium chloride

has also been extended to other systems which show a similar behaviour. Some typical cases are discussed below.

(a) **Phosphorus Pentachloride (PCl$_5$)**— Phosphorus penta-chloride which has a theoretical vapour density of 104·2 shows a vapour density varying with temperature and pressure ranging from nearly the theoretical value to half this value (see Table). This lowering of vapour density is explained by assuming the following process of dissociation:—$PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

DISSOCIATION OF PCl$_5$. ($PCl_5 \rightleftharpoons PCl_3 + Cl_2$)

Theoretical Density (air=1)= 7·2

Temp. °C	Density (air=1)	Percentage Dissociation
190°	4·99	44·3
200°	4·85	48.5
230°	4·30	67·4
250°	4·00	80·0
300°	3·65	97·3

A fraction of the gas dissociates under ordinary circumstances and this fraction gradually increases with temperature until the dissociation becomes almost complete above 300°C. As dissociation proceeds the colour of the gas gradually becomes more and more green due to the liberated chlorine. At every stage, until the dissociation is complete, the vapour contains molecules of chlorine, molecules of phosphorus trichloride and also undissociated molecules of phosphorus pentachloride.

(b) **Nitrogen Peroxide (N$_2$O$_4$)**—This substance offers a very interesting case of dissociation. At a low temperature, it is an almost colourless crystalline solid, which melts to a pale yellow liquid at 10°C. Its colour gradually gets darker as the temperature is raised and at 22°C. it boils giving off reddish brown vapours. On further raising the temperature the colour of the vapour darkens until at 140°C it assumes the maximum intensity of colour, becoming almost black. The reverse change takes place on cooling. Measurement of density of the gas shows that as the temperature rises the gas dissociates more and more forming NO$_2$ molecules according to the equilibrium, $N_2O_4 \rightleftharpoons 2NO_2$. The above change of colour is due to the fact that N$_2$O$_4$ molecules are colourless, while NO$_2$ molecules are dark brown and at any temperature the colour of the gas is determined by the proportion of each of these two gases present in the system. At 140°C the dissociation is almost complete and the colour is due to the NO$_2$ molecules only. The fall of vapour density with rise of temperature is shown in the accompanying table.

N_2O_4 DISSOCIATION, $N_2O_4 \rightleftharpoons 2NO_2$
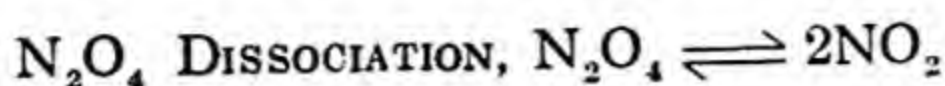
(Theoretical density = 46)

Temp. (°C)	Vapour density ($H_2 = 1$)	Degree of dissociation
15	41·0	12·2 per cent
35	36·22	27·0 ,,
65	28·25	62·8 ,,
100	24·3	89·5 ,,
140	23·02	almost 100·0 ,,

On further raising the temperature the density further falls and the intensity of colour begins to diminish until at 600°C the gas becomes colourless. These further changes are due to the dissociation of the NO_2 molecules into nitric oxide and oxygen according to the equation $2NO_2 \rightleftharpoons 2NO + O_2$, the dissociation being almost complete at 600°C.

Other examples of gaseous dissociation are those of hydriodic acid and of calomel according to the equation (i) $2HI = H_2 + I_2$ and (ii) $Hg_2Cl_2 = Hg + HgCl_2$ respectively. The latter dissociation is very interesting in the sense that since the dissociation is usually nearly complete, the observed vapour density will be half the theoretical value for Hg_2Cl_2 and so, unless the dissociation was suspected to occur it would seem that the molecules of calomel existed wholly as HgCl in the vaporous state. But, by diffusion experiments it was established that the vapour contains free mercury atoms and the real interpretation became then apparent. Such dissociation of heavier molecules into lighter ones is undergone not only by compounds but also by elements. Thus, the halogen molecules, sulphur, and many other elements dissociate at sufficiently high temperature into atoms.

Calculation of the Degree of Dissociation— Degree of dissociation of a vapour is the fraction of the total number of molecules which has suffered dissociation either expressed as a fraction or expressed in per cent by weight. The *degree of dissociation* of a substance can be calculated from the density of the vapour. The method of calculation will be shown in a definite case, say, PCl_5, but is valid for any substance, one molecule of which dissociates to give two molecules. The equation for the dissociation is $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

Let 1 mol of the pentachloride be vaporised and let a fraction α of it dissociate into the trichloride and chlorine (Fig. 17). Evidently, by the dissociation of α mols of pentachloride we shall get α mols of the trichloride and α mols of chlorine. Also, there would remain $1 - \alpha$ mols of undissociated pentachloride. Therefore, the total number of mols present in the system after dissociation is $(1 - \alpha) + \alpha + \alpha = 1 + \alpha$. So, due to dissociation the number of mols increases from 1 to $1 + \alpha$ and therefore the volume occupied by the system increases in the same proportion (since the volume V varies directly as the total number of mols n).

Therefore, if V_0 be the volume, which the system would have occupied had there been no dissociation and V, the actual volume of the vapour due to dissociation, we should have

Dissociated Vapour   Undissociated Vapour
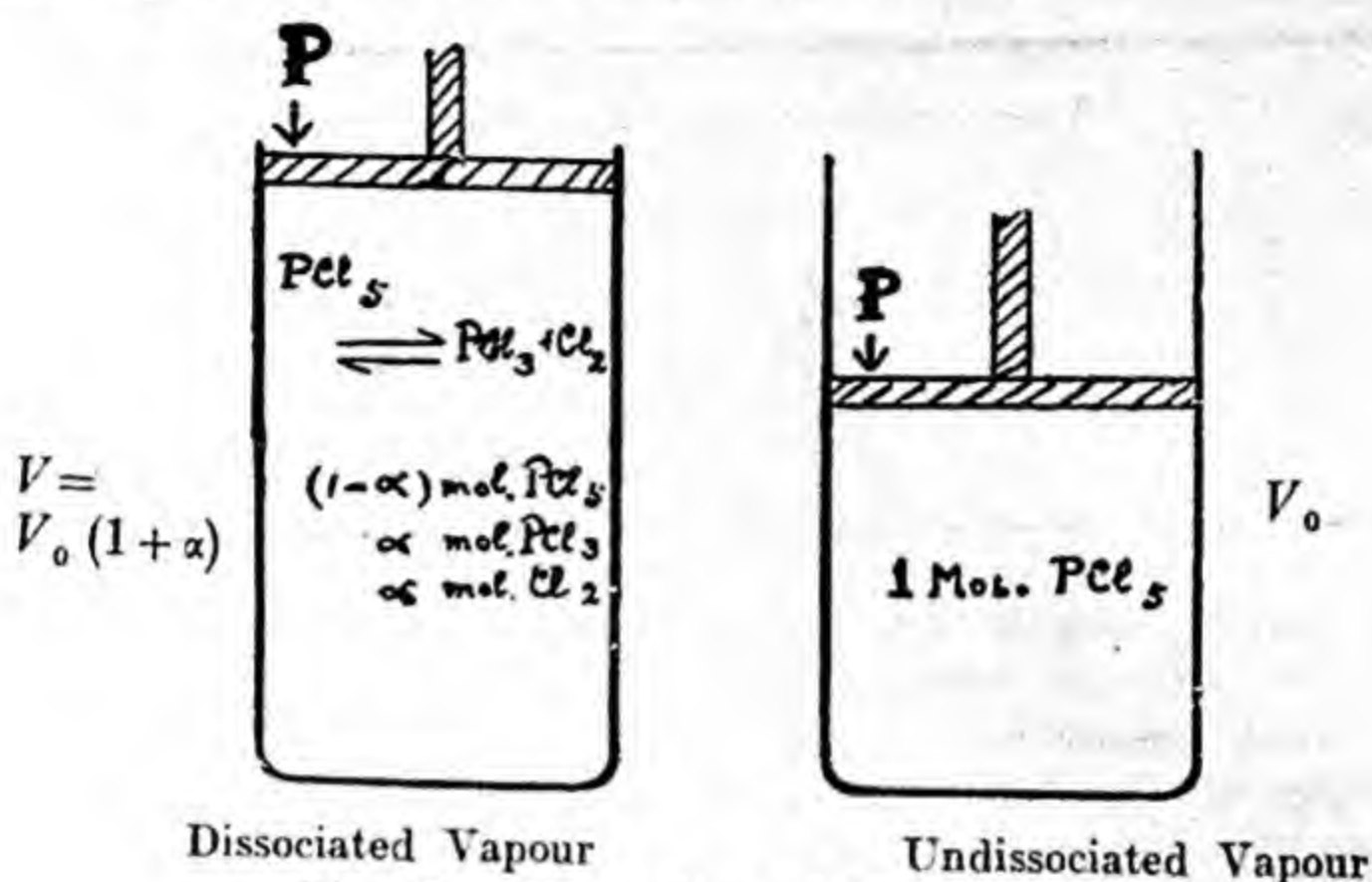
Fig. 17.—Dissociation of PCl_5 Vapour.

$$\frac{V}{V_0} = \frac{1+\alpha}{1} = \frac{d_0}{d} \text{ (since density } d \text{ is inversely}$$
$$\text{proportional to volume)}$$

Or $\qquad d_0 = d(1+\alpha)$

$$\therefore \quad \alpha = \frac{d_0 - d}{d} \quad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \quad (2)\text{-IV}$$

where $d_0 = theoretical$ density assuming no dissociation, and $d = observed$ density, both under the same pressure.

So knowing d, the actual density and d_0, the theoretical density (which is given by equation 1-(IV) in absolute units) the degree of dissociation α is easily calculated from the above equation. It remains to point out that d_0 and d are to be expressed in the *same system of units* either with reference to air or to hydrogen or in absolute units. Since pressure is proportional to the number of mols under constant volume condition, the above equation holds good if reciprocal of pressure is substituted for density. A typical example involving dissociation of iodine is illustrated in Example 3.

If one molecule of the substance dissociates into n molecules it can be shown by the same procedure that the equation becomes

$$\alpha = \frac{d_0 - d}{(n-1)d} \quad \cdots \qquad \cdots \qquad \cdots \quad (3)\text{-IV}$$

Association—So long we have been discussing cases of vapour density being lower than the theoretical value. But cases are on record where the vapour density is higher than what would be expected from their molecular formula, or in other words the vapour of one gm molecule of the substance occupies a volume less than 22·4 litres. Well-known examples of such abnormalities are water and acetic acid when their

density is measured nearabout their respective boiling points. If the temperature of the vapour is gradually increased, the vapour density slowly falls to the normal value where it remains fairly constant. It is assumed in these cases that a portion of the molecules of the vapour exists as double or more complex molecules, and the existence of these aggregates or clusters is responsible for the increased density. As the temperature rises these aggregates break down to form single undisso-ciated molecules. Evidences from other sources corroborate these con-clusions. This phenomenon is called molecular association in the gaseous state.

Other examples of association are the vapours of the chlorides of some metals such as aluminium, iron, beryllium, etc. whose vapour phase behaves respectively like Al_2Cl_6, Fe_2Cl_6, Be_2Cl_4, etc. Vapours of many elements for example, sulphur and phosphorus show different degrees of association at different temperatures.

EXAMPLE 2. *Calculate the percentage of NO_2 (i) by weight and (ii) by volume, in nitrogen peroxide (N_2O_4) of vapour density=35.*

$$N_2O_4 \Longleftrightarrow 2NO_2.$$
$$1-a \qquad 2a$$
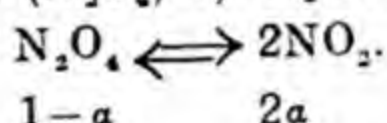
(i) From the equation, $d_0 = d(1+a)$.

where d_0=theoretical density=$\frac{1}{2}$ $(N_2O_4)=\dfrac{14\times2+16\times4}{2}=46$

and d=observed density=35.

We have $46=(1+a)\,35$ or $a=0.314$.

Total fraction of mols decomposed to form NO_2 molecules $\Big\}\; \begin{aligned} &=0.314 \\ &=31.4 \text{ per cent.}\end{aligned}$

∴ the percentage of NO_2 by weight$=31.4\%$. This is evidently also the degree of dissociation.

(ii) Since volume is directly proportional to the total number of mols, we have,

Volume of NO_2 is proportional to $2a$.

Volume of N_2O_4 . . . . . . $(1-a)$.

Total volume is . . . . $1-a+2a=1+a$.

Percentage of NO_2 by volume=

$$100\times\frac{2a}{1+a}=\frac{100\times0.628}{1.314}=47.8\%$$

Percentage of N_2O_4 by volume=

$$100\times\frac{1-a}{1+a}=100\times\frac{1-0.314}{1+0.314}=52.2\%.$$

EXAMPLE 3. *0.891 gm. of iodine vaporised at 1001°C in an one litre quartz flask registers a pressure of 0.4742 atmosphere. Calculate what fraction of iodine molecules is present as atoms.*

Since pressure is proportional to the number of mols and since pressure, $P=cRT$ we should have,

$$1+a=\frac{P_{obs}}{P_0}=\frac{P_{obs}}{cRT}$$

where $c=(0.891/2\times127)$ mols/litre

$$\therefore\; 1+a=\frac{0.4742\times2\times127}{0.891\times0.0821\times1274}=1.283$$

$$\therefore\quad a=0.283 \text{ or } 28.3 \text{ per cent.}$$

The iodine molecules are 28.3 per cent dissociated into atoms $(I_2 \Longleftrightarrow 2I)$ under the given conditions.

EXERCISES

1. Describe briefly the different methods of determining the vapour density of gases and liquids.

2. Describe in details the Victor Meyer's method of determining the molecular weight of a volatile liquid.

3. Density of a gas varies with temperature, but not the vapour density—Explain this statement. Are there any exceptions? What theories have been advanced to explain these anomalies.

4. What is meant by the statement ammonium chloride has an abnormal vapour density? Can you advance any theory as an explanation for this fact, noting at the same time experimental evidences in your support? Give instances of two other substances which have got abnormal vapour densities.

5. Describe the effect of heat on the following substances—Ammonium chloride, Phosphorus pentachloride.

6. How do you determine the molecular weight of the following substances :—Acetone, vapour of zinc, mercury vapour, oxygen, ether and chloroform.

7. Hydriodic acid when heated dissociates into hydrogen and iodine $(2HI \rightleftharpoons H_2 + I_2)$. Will it show abnormal vapour density? Give reasons for your answer.

8. In the determination of the molecular weight of chloroform vapour by Hofmann's method the following results were obtained : weight of liquid 0·2704 gms; volume of vapour, 113 c.c.; temperature of vapour. 99·6°C; atmospheric pressure, 747 mm.; height of mercury in the tube 285·2 mm. Calculate the molecular weight of chloroform. [120·3]

9. The following data were obtained in determining molecular weight of benzene by Dumas method using a bath at 100°C :—wt. of bulb in air—29·1840 gm ; wt. of the sealed bulb containing benzene—29·3458 gm.; wt. of the bulb filled with water of density 0·998—144·1 gm. ; atmospheric pressure—760 mm. Density of air at N.T.P.—0·001293 gms per cc. ; Room temperature −25°C. Calculate the molecular weight of benzene. [79·5]

(*Hints* :—Apply buoyancy correction to the weight of benzene *i.e.* add to its apparent weight, the weight of an equal volume of air. This correction cannot be neglected here being nearly half the weight of benzene).

10. Calculate the vapour density of a substance from the following data :—0·16 gm. substance on vaporization displaces 26·2 c.c. moist air at 17°C and 764 mm. (Tension of aqueous vapour at 17°C = 14 mm). [73·9]

11. 0·0623 gms. of a substance gave by Victor Meyer's method 31·5 c.c. of air measured at 15°C and 750 mm. Find the mol. wt. of the substance. Tension of aqueous vapour at 15° = 12·7 mm. [48]

12. The following observations were made in a Victor Meyer determination :

Weight of liquid used = 0·0572 grams.
Volume of dry air displaced = 15·3 c.c.
Room temperature = 23·5°C.
Barometric pressure = 763·2 mm.

Calculate the mol. wt. and density at N.T.P. of the vapour.
[90·6 : 0·00403]

13. Ammonium chloride when vaporised at 580°C and 813·8 mm pressure has a density of 0·6257 gm per litre. Calculate the degree of dissociation. [70·8%]

14. At 60°, the vapour density of nitrogen peroxide is 30·2. Calculate the percentage of NO_2 molecules (a) by volume. (b) by weight.
[(a) 68·7%. (b) 52·3%]

15. When PCl_5 is heated, it gassifies and dissociates into trichloride and chlorine. At 182°C the density of the gas mixture is 73·5 while at 200°C it is 62. Find the degree of dissociation at 182° and 200°C (P=31).

[41·6% ; 68·0%]

16. 0·874 gms. of iodine displaced 137 c.c. of air measured at 21·5°C and 723 mm. Calculate the vapour density of the iodine and the degree of dissociation at the temperature of the experiment. (I_2=I+I). [0·569]

17. 4·5 gms. of PCl_5 were completely vaporised at 252°C, the vapour occupied 1700 c.c. at one atmosphere. Calculate the degree of dissociation at the temperature (P=31, Cl=35·5).

[82·4%]

18. Write explanatory notes on 'Abnormal vapour Density.'

19. Describe Pebal and Than's experiments on the dissociation of ammonium chloride. At 90°C the vapour density of nitrogen peroxide (N_2O_4) is 24·8 (referred to H_2=I). Calculate the degree of dissociation into NO_2 molecules at this temperature.

[85·4%]

20. Under what conditions is Avogadro's law strictly applicable ? State the principles involved in the accurate determination of atomic and molecular weights by the gas densities.

21. A gas of known molecular weight is found to deviate widely from the ideal gas equation, which may be due to either dissociation or non-conformity with ideal gas equation. What experiments would you make to ascertain the real cause of this deviation.

22. A one-litre vessel contains NO at 25°C and 200 mm pressure. A small bulb containing 0·5 gm bromine is broken inside the vessel and the pressure is found to be 250 mm. If only NO, Br_2 and NOBr be present in the vessel calculate the partial pressure of each in the equilibrium system.

[P_{NO}=183·8 ; P_{BR_2}=50·0 ; P_{NOBr}=16·2 mm]

23. In the equation $M = \dfrac{dRT}{P}$ if R be expressed in calories per degree and P in atmospheres, in what unit should d be expressed?

[gm-atm/cal. i.e. gms per 41·5 c.c.]

24. Indicate a simple experimental device by which pure HD can be distinguished from an equimolecular mixture of H_2 and D_2, where D stands for deuterium i.e. heavy hydrogen.

CHAPTER V

GAS—LIQUID TRANSITION. THE LIQUID STATE

Properties of Liquids.—Besides the evident distinction that liquids occupy a definite volume under given conditions whereas gases fill up all the available volume, in also most other physical properties liquids are well-differentiated from gases. Thus, liquids have far greater density than gases; roughly speaking, liquids are about one thousand times as dense as gases. The difference is much more marked in point of compressibility as liquids are well over ten thousand times less compressible than gases.

It is remarkable, however, though not often realised that liquids, though having much stronger intermolecular attraction than gases, have a co-efficient of cubical expansion on heating of the same order, sometimes as high as one-third, as that of permanent gases. For example, one litre of a gas at N.T.P., when heated through 1°C, expands by 3·66 c.c. whereas one litre of pentane or acetone under identical conditions shows an expansion of as high as about 1·5 c.c.

Fundamentally, however, there is no basic distinction between the liquid and the gaseous state as can be easily seen from the fact that one can imperceptibly pass from the one state to the other without even passing through the phenomenon of condensation. This will be discussed later under the section entitled, 'Continuity of State'.

The Nature of Liquids—Since liquids stand midway between solids and gases, the liquid state may be expected to possess properties intermediate between these two states, which in some measure it has. Fundamentally speaking, however, since an ideal gas is matter in complete disorder on a molecular scale, and a perfect solid is matter whose molecules are completely well-ordered (zero entropy), liquids standing midway should be a compromised blending of order and disorder. In fact, evidences from all sources show that liquids have some degree of order, though very rudimentary, as if "the memory of the solid state persists in the liquids", and hence the modern tendency is to treat the liquid at least near its melting point as an extension of the solid state i.e. as a disordered crystal or, a crystal with short range order and long range disorder. The same reason makes it also attractive as an alternative to treat liquids at least near the critical point as imperfect gases. So, liquids are theoretically treated either as a disordered solid or as a condensed gas and both these approaches are of importance.

Of course, the very fact that liquids are formed show that there is strong intermolecular attraction as otherwise the kinetic energy of the molecules would have dispersed the liquid into a gas. Not much is known however about the values of these intermolecular forces, which act between neutral molecules and cause them to deviate from perfect gas law and ultimately bring about their condensation to the liquid state. The existence of these intermolecular forces was first envisaged by van der Waals

in his famous equation of state and so these forces are generally called **van der Waals forces.** The molecules in a liquid owing to their close proximity to each other are subject to these strong intermolecular forces which restrict their free motion, about the details of which very little is known

Owing to this unsatisfactory state of our theoretical knowledge about liquids, very little basic knowledge has been gained about them ; yet, the masterly researches of the investigators of the last century have done much to add to our knowledge about liquids and to show conclusively their close relationship with gases.

Continuity of State : Andrews' Experiments —Andrews (1861-1870) studied the effect of increasing pressure on gaseous carbon dioxide at different temperatures. His results are shown graphically in the accompanying diagram (Fig. 18), where the pressure is plotted against the volume ; each curve thus obtained is called an 'isothermal', as it applies to the gas at any particular temperature.
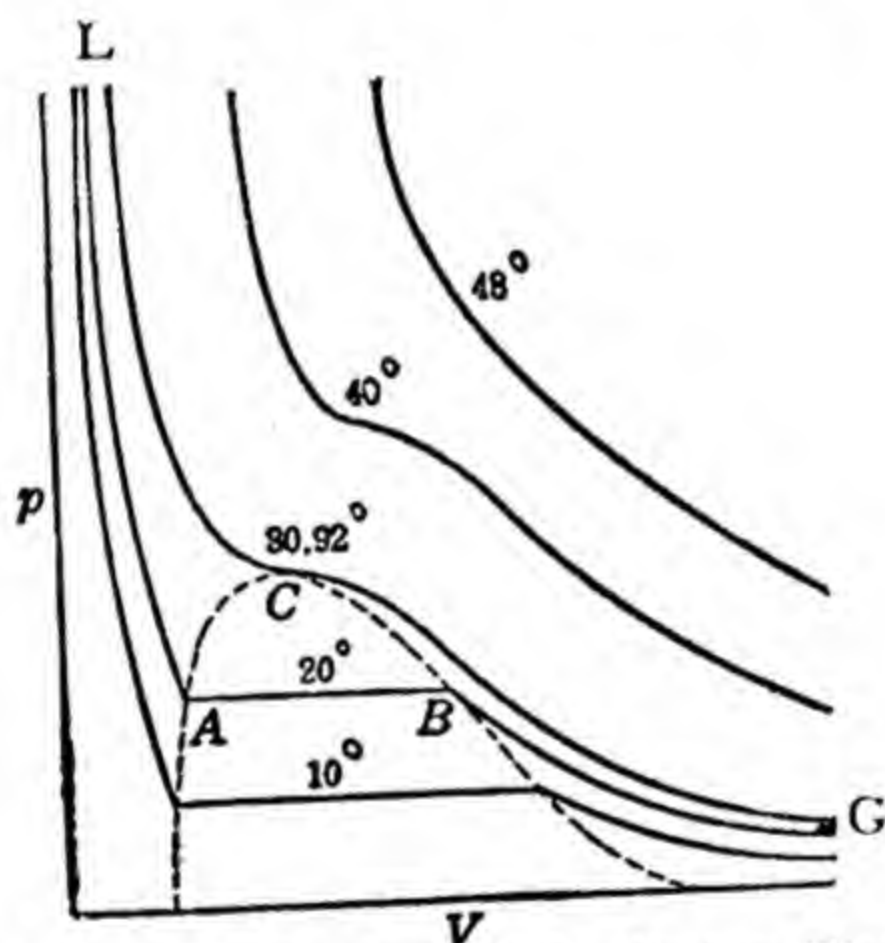
Fig. 18—Andrews Isothermals for Carbon Dioxide

The isothermal, GBAL represents the pressure-volume relation of carbon dioxide at 20°C, and following it we find that the volume of the gas gradually decreases with increasing pressure. At B, condensation to liquid state begins and since a liquid in contact with its saturated vapour has a constant vapour pressure, the curve follows a horizontal course until the point A is reached where all the gaseous CO_2 has been converted into the liquid state. The point B, therefore, stands for saturated vapour at 20°C and the point A represents the same wholly converted into the liquid state and any point between A and B represents a mixture of liquid and vapour under their saturation pressure at that temperature. The points B and A differ only in volume but not in pressure corresponding to the well-known fact that during condensation at constant temperature the vapour pressure does not change, i.e. the saturation pressure is constant at

constant temperature and is independent of the total quantity of the liquid. The portion of the curve between A and L represents the behaviour of liquid CO_2 under increasing pressure, and is very steep due to the fact that liquids are much less compressible in comparison with gases. The portion AB may therefore be looked upon as a connecting link between the isothermals of gaseous and liquid carbon dioxide at 20°C.

Now, as the temperature is raised the horizontal portion AB gradually shortens until at 31°C, it just vanishes, the isothermal at this temperature having a slight hump (inflexion point). Above this temperature there is even no trace of the horizontal portion AB, and no formation of liquid *i.e.* no separation of a separate distinguishable liquid phase however high the pressure, is observed. The isothermal curves are smooth figures (rectangular hyperbola) corresponding more or less to Boyle's law. Since existence of the straight portions like AB implies condensation, it is thus definitely established that there exists a temperature (31°C for CO_2), above which a gas cannot be liquefied however great the pressure may be ; this temperature is called the **critical temperature.** Gases at temperatures below the critical temperature are usually referred to as *vapours.* The pressure which is just sufficient to liquefy the gas at critical temperature is called *critical pressure*, and the volume occupied by *one gram mol* of the gas at critical temperature and pressure is called the *critical volume.*

The critical constants of different gases vary greatly as shown in a table to follow. It has been found that the extremities of the horizontal portions of the isotherms (*i.e.* points A and B) lie on a parabola (the dotted curve in the figure), the apex of which C necessarily lies on the critical point.

Continuity of State—From Andrews' experiments, it is apparent that there is no fundamental distinction between a liquid and a gas. It will be seen from the isotherms that a highly compressed gas is more akin in its physical properties to liquids than to gases. Even we can pass from the typical gaseous to the typical liquid state without passing through the phenomenon of condensation. It is evident from Figure 18 that there exists any number of paths connecting any point on BG (a typical gas) to any point on AL (a typical liquid), and if this path does not pass through the dotted region—which only denotes a vapour and a liquid in equilibrium—there will nowhere be an abrupt change in state though we started with a gas and finally got a liquid. To be more definite, if we have some gaseous carbon dioxide at a temperature represented by the point G and heat it at constant volume above 31°C to attain the same pressure as the point L and then cool the gas at constant pressure we ultimately obtain liquid carbon dioxide corresponding to the point L but since in this process we have nowhere passed through the dotted region we have never the liquid and the vapour co-existing. It is actually impossible to detect at what point the gas has been liquefied.

GAS-LIQUID TRANSITION This phenomenon illustrates the term, *continuity of state.*

Critical Phenomena in the Light of van der Waals equation—
The isothermals of gases near the critical condition as obtained by Andrews for carbon dioxide can be well interpreted by the van der Waals equation. Isothermals for carbon dioxide constructed from values calculated from van der Waals equation with suitable values for the constants a and b—sometimes called van der Waals isotherm in the p,v-plane for evident reasons—are shown in the figure (Fig. 19). It would be observed that these theoretical curves resemble the experimental curves very closely except for an S-shaped portion in the region of condensation. Of course, experimentally we cannot realize this S-shaped portion as the middle part of this portion signifies a hypothetical substance which expands in volume on increase of pressure, and what we actually observe is a horizontal line dividing the S-shaped portion into two loops of equal area.

If we expand and rearrange the terms in the van der Waals equation in descending powers of V we get a cubic equation in V as shown below.

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \left(\frac{a}{P}\right)V - \left(\frac{ab}{P}\right) = 0 \qquad \cdots \ (1)$$

This is in agreement with the fact that any horizontal line cuts the van der Waals curve at three points. As we raise the temperature these three points get closer and closer to one another and coalesce into one value at critical temperature. This means algebraically that if V_c is the critical volume, $(V - V_c)^3 = 0$, because this is the cubic equation which has three equal, real and positive roots. Expanding this we get
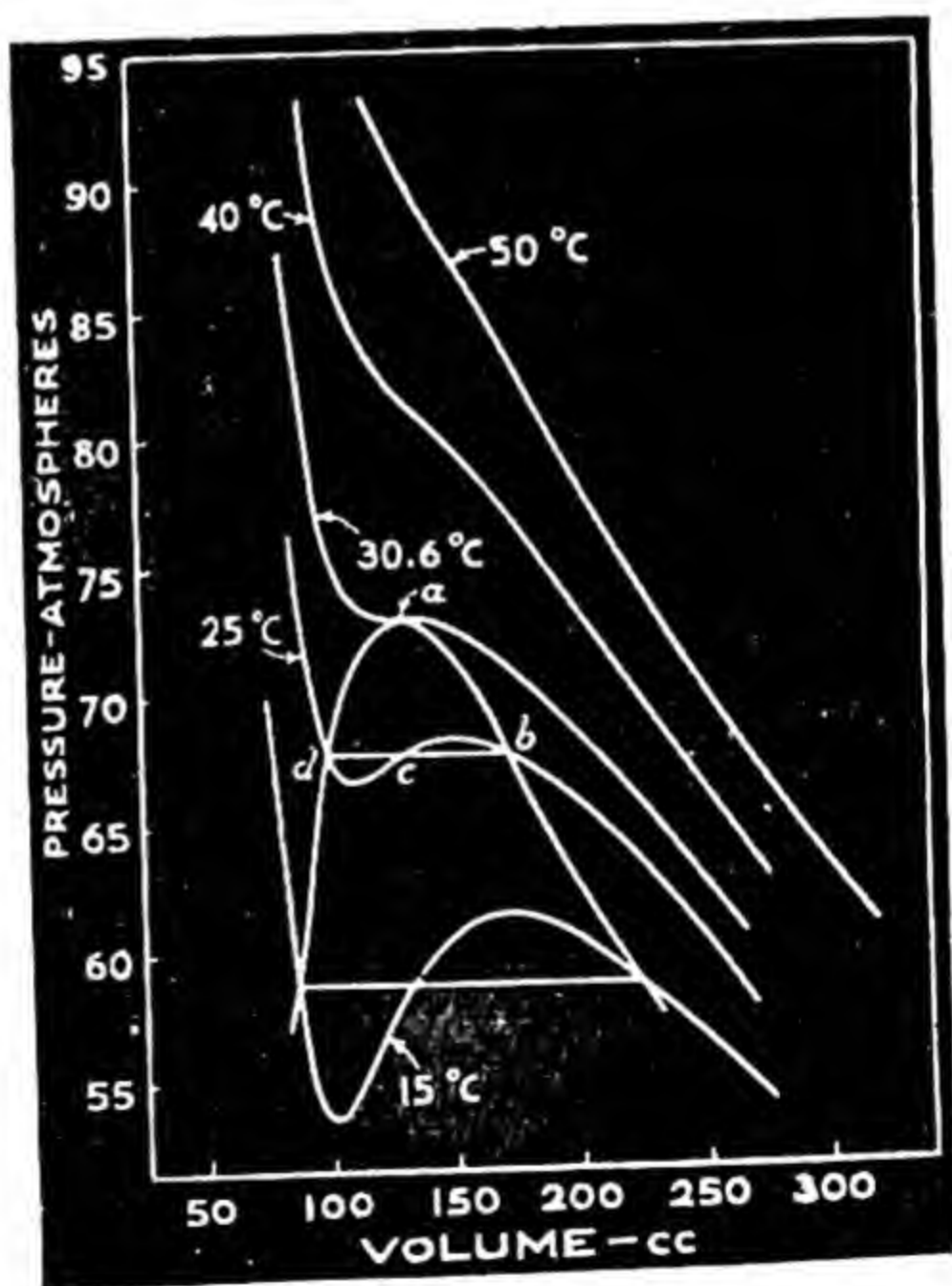

Fig. 19—Isothermals of CO_2 according to Van der Waals Equation

$$V^3 - (3V_c)V^2 + 3(V_c)^2 V - V_c^3 = 0 \qquad \cdots \qquad \cdots \ (2)$$

4

Since this equation is identical with equation (1) under critical conditions, we can equate the coefficients of similar terms according to a standard process of algebra and get,

$$3V_c = b + \frac{RT_c}{P_c} \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \quad (3)$$

$$3V_c^2 = \frac{a}{P_c} \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \quad (4)$$

and $V_c^3 = \frac{ab}{P_c} \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \quad (5)$

where the subscript c indicates critical condition values.

Equations (4) and (5) on rearrangement give

$$a = 3V_c^2 P_c \quad \text{and} \quad b = \tfrac{1}{3}V_c \qquad \ldots \qquad \ldots \quad (6)$$

Since V_c for a gas is not known as accurately as P_c and T_c it is better to express a and b in terms of P_c and T_c which can be readily done by eliminating with the help of equation (3) when we get,

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad \text{and} \quad b = \frac{RT_c}{8P_c} \ldots \qquad \ldots \qquad \ldots \quad (7)$$

These equations can be used either to calculate a and b from critical data, or to calculate the critical data from a and b. Further, by eliminating a and b we get the equation,

$$R = \frac{8}{3} \frac{P_c V_c}{T_c} \quad \text{or} \quad \frac{RT_c}{P_c V_c} = \frac{8}{3} \qquad \ldots \qquad \ldots \qquad \ldots \quad (8)\text{-V}$$

which means that for all gases the ratio $P_c V_c / T_c$ is a constant equal to 3/8 times the value of R. Experimentally, however, it is found to vary from gas to gas. For most gases and liquids $RT_c / P_c V_c$ has not the theoretical value 2·67 but generally lies between 3 and 4 (see table on P. 52). It is really gratifying to note that though the critical constants vary over a wide range the above ratio as expected from the van der Waals equation is nearly constant at a value fairly close to the predicted value. In fact all the above theoretical equations involving critical constants are only approximately true and leave much to be desired in point of quantitative agreement with observed data, which is due to an inadequacy of the van der Waals equation.

The Principle of Corresponding States —If we substitute in the van der Waals equation the values of a, b and R as obtained above, we get,

$$\left(P + \frac{3V_c^2 P_c}{V^2}\right)\left(V - \frac{V_c}{3}\right) = \frac{8}{3}\frac{P_c V_c T}{T_c}$$

Dividing the first factor by P_c and the second factor by V_c in the left-hand side and by $P_c V_c$ in the right-hand side,

$$\left(\frac{P}{P_c} + \frac{3V_c^2}{V^2}\right)\left(\frac{V}{V_c} - \frac{1}{3}\right) = \frac{8}{3}\frac{T}{T_c}$$

or $\left(P_r + \frac{3}{V_r^2}\right)\left(3V_r - 1\right) = 8T_r \qquad \ldots \qquad \ldots \quad (9)\text{-V}$

where $P_r = \dfrac{P}{P_c}$, $V_r = \dfrac{V}{V_c}$ and $T_r = \dfrac{T}{T_c}$ *i.e.* the subscript *r*

stands for the relative value with respect to the critical condition. It should be noted that P_r, V_r and T_r are dimensionless quantities and further, that the form of the above equation is similar to that of its progenitor, *viz.* the van der Waals equation. Such transformation is possible for any equation which contains only three constants.

This equation is called the *equation of corresponding states* or *the reduced equation of state*. The most important thing to note here is that the reduced equation contains no constant characteristic of any individual gas and so would be applicable to all liquids and gases. Expressed physically this equation means that when two gases are equally removed from their critical temperature and pressure, they must occupy the same fraction of their respective critical volumes. This equation is however found to be only approximately valid for real gases.

Experimental Determination of Critical Constants—The existence of critical temperature was established by Cagniard de la Tour in his experiments on ether but it was not until the above work of Andrews on CO_2 that any significance was attached to this important observation. The determination of critical constants can be roughly made with his apparatus (Fig. 20). De la Tour's apparatus consists of a hermetically sealed thick-walled glass tube, one limb of which contains the liquid in contact with its saturated vapour and at the top of the other limb is enclosed a known volume of air, the rest being filled with mercury. The apparatus as a whole is placed in a bath, whose temperature is gradually raised. At a certain temperature, the surface of separation between liquid and vapour suddenly vanishes and the whole mass of vapour and liquid becomes homogeneous.

If the bath is cooled, the reverse phenomenon happens; at a certain point a liquid mass suddenly appears in a misty form and two distinct layers of gas and liquid again separate. This temperature at which the surface of separation between the liquid and vapour disappears on heating and reappears on cooling, is the *critical temperature*. Just before the surface of separation vanishes a peculiar phenomenon happens; the whole mass of liquid and vapour seems to have a kind of very fine opalescence which

Fig. 20—Critical State

scatters light beautifully; this is called critical opalescence. The *critical pressure* is also measurable by this apparatus, the enclosed air serving as a manometer.

The reason for the disappearance of the surface of separation is due to the fact that with the rise of temperature the density of the liquid decreases while the density of the vapour
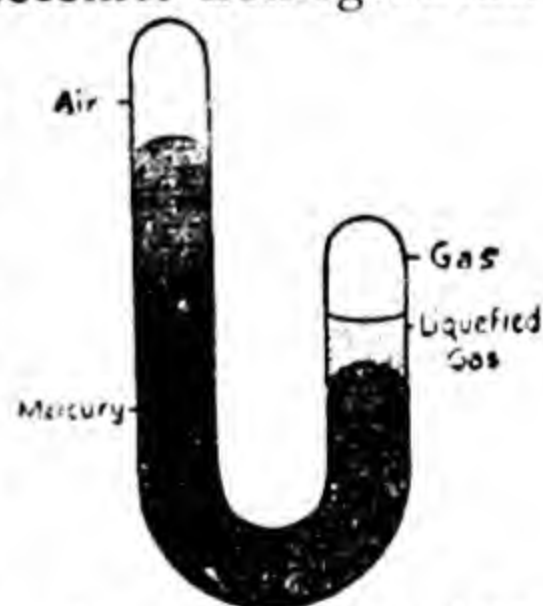
above the liquid increases and at critical temperature and critical pressure, the densities of the liquid and the vapour become equal and so one is indistinguishable from the other. In fact, not only density but all physical properties of the two states become identical at the critical point.

Determination of Critical Density—The above apparatus is not quite suitable for determination of critical density. In fact, a direct experimental determination of the same is liable to large error. A graphical method, called *Cailletet and Mathias Method*, is generally used.

The method depends on the empirical rule, first proposed by the above authors that the mean density of any liquid and its co-existing vapour is linear with temperature. So, the density of a liquid and of the vapour in equilibrium with it, is experimentally determined at a number of temperature near critical point, and these densities are plotted against temperature to form a closed curve as shown in the figure. The average of the two density values at each temperature is also plotted and a straight line is extrapolated to cut the foregoing closed curve at the critical point, and this extrapolated density is the *critical density* and its reciprocal is the *critical volume* per gram.

Fig. 21—Determination of Critical Density by Cailletet and Mathias Method.

Some representative values of critical constants including molar critical volumes are compiled in the following table.

CRITICAL CONSTANTS

Substance	$T_c °K*$	$P_c atm.$	$V_c c.c.$	$\dfrac{RT_c}{P_c V_c}$
Helium	5·2	2·25	61·5	3·08
Hydrogen	33·2	12·8	69·7	3·05
Argon	150·7	48·0	77·1	3·35
Nitrogen	126	33·5	90·0	3·42
Oxygen	154·3	49·7	74·4	3·42
CO₂	304·2	72·8	94·2	3·64
Ammonia	405·5	112·2	72·0	4·12
Benzene	561	48·0	256·0	3·75
Acetic Acid	594·7	57·1	171·2	4·99
Acetonitrile	547·8	47·7	173·1	5·45

* Note that °K means degree Kelvin and is simply another name for temperature in the absolute scale.

Critical Point or Critical Region : Some Recent Experiments—
We have assumed in the de la Tour's experiment that the temperature at which the meniscus becomes indistinguishable is the critical temperature where the liquid and the vapour become identical in property. Some recent experiments by Mass and others have brought to light some interesting features at the critical point which show that there is a small "spread" near the critical point. A very interesting fact is that when the meniscus has just disappeared, if a delicate quartz spring with a small load is placed in the vapour and the liquid phase respectively, it experiences a difference in buoyancy showing that there is still a difference in density between the two regions. Another very peculiar observation is that very near the critical temperature the meniscus has a tendency to disappear and reappear at the same place in a tube even though it is made upside down after the disappearance of the meniscus. All these facts show that the liquid state has a tendency to persist its molecular clusters over a short range above the temperature at which the meniscus disappears, but the existence of a true critical temperature is however definite and cannot be doubted.

Three states of Matter : Inadequacy of this Concept—
Nature has a subtle way to rebel against any conformity imposed on her by man-made classification. Thus, ordinarily, matter has to be either a solid or a liquid or a gas with the familiar properties. However, helium when cooled to very low temperature (below $-271°C$ $i.e.$ below $2°K$), is outside this scheme. Under such conditions it is much less viscous than a gas, fills a vessel like a liquid sometimes creeping up along the side and over down the edge, and conducts heat much better than even many metals. Helium in this fascinating state of matter is called Helium II. Another such bizarre phenomenon is the possibility for a liquid and its vapour to coexist in equilibrium under such compression that the vapour is denser than the liquid. Quite a few such systems usually consisting of mixtures have been observed to exist under high pressure so that a 'gas' bubble could be made to rise or sink at will through the liquid by a change of pressure. It is quite likely that far out in space many unfamiliar and unknown states of matter beyond our conventional classification exist and the present classification is neither exhaustive nor absolute.

Liquefaction of Gases—Attempts to liquefy gases were made early in the eighteenth century and some success was attained by earlier workers who had liquefied easily liquefiable gases like ammonia, sulphur dioxide, etc. But sometimes their conclusions were erroneous as they were at times liquefying only the water-vapour in the gas, which was retained in the gas due to imperfect drying.

In 1805 Northmore liquefied chlorine and sulphur dioxide

by applying pressure but failed with CO_2 since his apparatus could not stand the high pressure required for this purpose. In 1823 Faraday began systematic researches in this field and was successful in liquefying all gases which require only moderate pressure and not very low temperature for condensation. His method was very simple indeed; he generated the gas in an inverted U-shaped tube by heating a suitable solid placed in one branch of the tube and immersed the other end in a freezing mixture. When the pressure inside becomes sufficiently high, the gas is liquefied in the cooler arm of the tube. In this way Faraday liquefied sulphur dioxide, hydrogen sulphide, carbon dioxide, nitric oxide, cyanogen and ammonia.

Fig. 22—Faraday's Method of Liquefaction of Gases

The next important worker was Thilorier (1834) who liquefied carbon dioxide and even solidified it as a snow-white mass by allowing the liquid carbon dioxide to evaporate freely. He also found that a mixture of solid carbon dioxide (dry ice) and ether evaporating under reduced pressure could produce a temperature as low as $-100°C$, and this was used as a freezing mixture under the name of 'Thilorier mixture.'

Up till then, certain gases amongst which were hydrogen, oxygen and nitrogen could not be liquefied even by application of enormous pressures, sometimes up to 3000 atmos and were designated as 'permanent gases.' They were not long to remain so, for in the year 1877 Cailletet and Pictet succeeded in liquefying oxygen and air by submitting them to a pressure of 300 atmospheres and using liquid SO_2 evaporating under reduced pressure as refrigerant.

Andrews' Discovery of Critical Temperature—In the mean time (1870), Andrews' experiments on the liquefaction of carbon dioxide, which have been already discussed. (P. 47) furnished the most fundamental knowledge on liquefaction. His experiments clearly demonstrated that for any gas there exists a temperature called its critical temperature below which it can be liquefied by the application of appropriate pressures, but above this temperature the gas stubbornly resists all attempts towards condensation.

Joule-Thomson Effect or Adiabatic Expansion—Joule and Thomson showed that if a gas under pressure is forced out through a porous plug, the gas suffers a fall in temperature and this phenomenon is known as *Joule-Thomson effect*. Joule-

Thomson effect depends upon the fact that all gases are ordinarily imperfect or, looking from the kinetic point of view, the molecules attract each other. So, if a highly compressed gas expands against a low pressure in such a way that *it performs no external work*, the energy required to increase the average distance of the molecules from one another is absorbed from the gas itself and so the gas falls in temperature. The discovery of this effect served as a powerful weapon in the hands of later workers to liquefy all the gases which had still escaped liquefaction (also, *vide* Ch. VIII).

The theoretical principles being thus established by Andrews and by Joule and Thomson, then followed an era of busy work when scientists were engaged in liquefying the most obdurate gases as hydrogen and helium, and technical chemists were engaged to conduct this liquefaction on a large scale.

The boiling points of a number of common liquefied gases are given in the following table.

Substance	B. P. °C.	B. P. °Abs	Substance	B. P. °C.	B. P. °Abs.
Sulphur Dioxide	−10·1	262·9	Argon	−185·7	87·3
Ammonia	−33·5	239·5	Air	−193·1	79·9
Chlorine	−34·6	238·4	Nitrogen	−195·7	77·3
Ethane	−161·4	111·6	Hydrogen	−252·7	20·3
Oxygen	−182·9	90·1	Helium	−268·9	4·1

Manufacture of Liquid Air— Hamson in England and Linde in Germany were successful in erecting large scale plants for the liquefaction of air. These machines utilised Joule-Thompson effect coupled with method of regenerative cooling as explained below.

*Principle of Regenerative Cooling—*For most gases cooling by Joule-Thompson effect is very small. For example, air at 20°C by falling from a pressure of 50 atmospheres to 1 atmosphere suffers a temperature drop of about 12°C. But this drop in temperature may be intensified if the gas already cooled by Joule-Thomson effect is circulated round the incoming gas so that it gets cooled and so undergoes the Joule-Thomson expansion at a lower initial temperature. A further drop in temperature occurs to the incoming gas, and this cooler gas is employed to cool further another portion of the incoming gas, which becomes still more cooled by the subsequent Joule-Thomson expansion passing through the valve. Thus the cooling effect gradually accumulates and as a result of this *cumulative cooling* effect the gas ultimately cools to its liquefying temperature. The efficiency of this method of regenerative cooling is assisted by the fact that the lower is the initial temperature of the gas, the greater is the magnitude of the Joule-Thomson cooling.
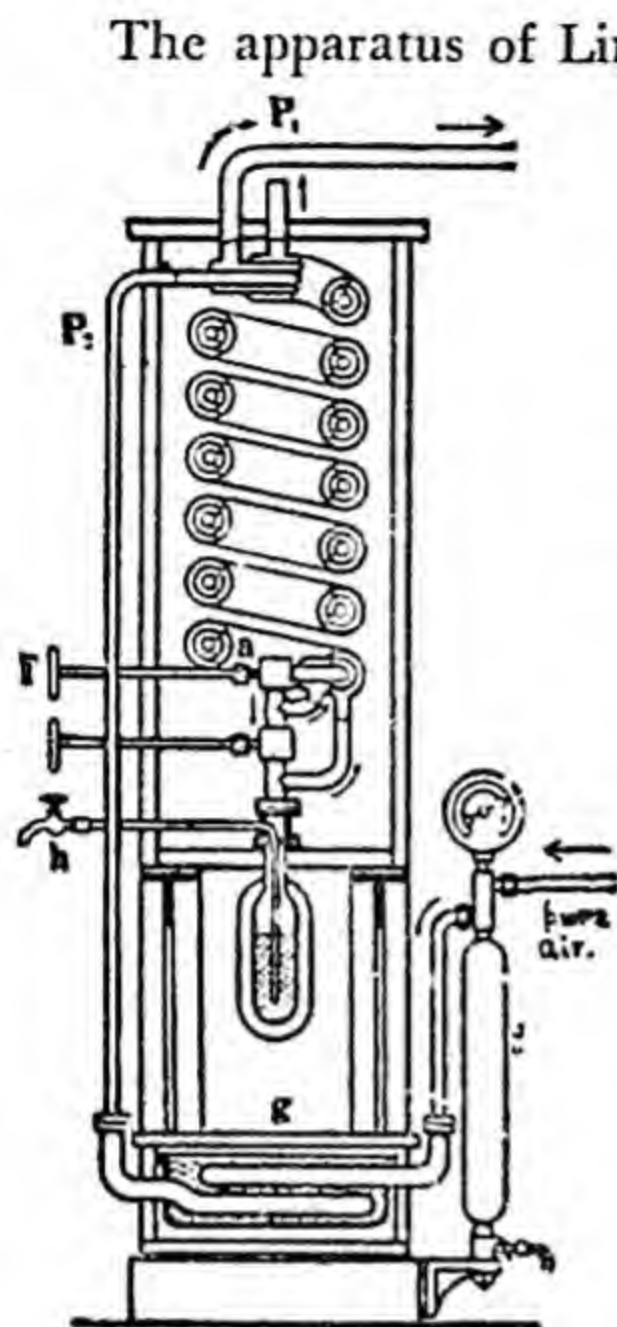
The apparatus of Linde is shown diagramatically in Fig. 23.

Fig. 23—Linde's Apparatus

The air freed from carbon dioxide and moisture which would otherwise choke the apparatus is first cooled at $-20°C$ by passing through a freezing mixture and is then forced through the inner tube of two or three concentric pipes at a pressure of about 200 atmospheres. This tube is hundreds of yards long and is coiled spirally to save space. By regulating the throttle valve, operated by the handle T, the air is allowed to expand suddenly in a chamber to a pressure of about 20 atmospheres. By this sudden expansion the air falls in temperature to about $-78°C$ due to Joule-Thomson effect and this cooled air passes back through the outer tube. The incoming air is thus cooled by conduction by the outgoing air before it expands and this cooled air falls lower down in temperature by expanding through the valve, and then passes away through the outer-tube. Thus there is a *cumulative cooling effect* as a result of which the incoming air gets sufficiently lower in temperature. The second throttle valve is then opened and the already cooled air gets liquefied by expansion through this valve to one atmosphere. The air that passes through the apparatus goes back to the pumps, where it is compressed to 200 atmospheres and re-circulated. When sufficient amount of liquid air is collected it is siphoned out through the side tube. To minimise the absorption of heat from outside, all parts of the apparatus are surrounded by insulating materials, viz. felt, wool, feathers, etc.

More efficient liquid air machines (*e.g.*, Claude's process, etc.) have now come in use which instead of solely employing Joule-Thomson effect make the compressed gas also do work by expansion against external pressure and thereby suffer cooling. The industrial importance of oxygen and nitrogen for chemical industries has led to the development of machines where fractionation and liquefaction go on simultaneously and continuously. The fractionation is usually effected by rectifying columns, down which liquid air trickles and meets an up-going stream of air. Nitrogen (B.P., $-194°C$) being more volatile than oxygen (B.P., $-182°C$), the vapour which passes out from the top is nitrogen with a small percentage of oxygen while the liquid which collects at the bottom is nearly pure oxygen.

Since there is a commercial demand for argon and neon, the former for use in gas-filled lamps and the latter in coloured

lights of the gas-discharge type (*neon sign*), these two gases are prepared by liquid air manufacturers. These gases since they are more volatile than oxygen or nitrogen remain in that portion of the compressed air which escapes liquefaction. This portion is withdrawn, liquefied and submitted to fractional distillation to be purified from admixed nitrogen. Helium and neon are then separated by treatment with cool activated charcoal, the separation being based upon the fact that neon is more strongly adsorbed.

For commercial refrigeration *e.g.* refrigerators, air-conditioning, etc., the employment of suitable gases in the liquefied state is being rapidly developed; for this purpose, ammonia, sulphur dioxide, methyl chloride, the newly developed CF_2Cl_2 (commercially called freon or arcton), etc. are extensively used. The last named gas, *i.e.* CF_2Cl_2 is almost ideal for commercial refrigerators as it is odorless, non-toxic, non-corrosive, inert and very stable, and has excellent thermodynamic properties.

Solid carbon dioxide under the trade-name "*dry ice*" also commands a large sale for ordinary refrigeration. Solid carbon dioxide has the peculiar property of directly passing into vapour without going through the intermediate stage of liquefaction because its vapour pressure reaches one atmosphere at $-79°C$ which is lower than its melting point, $-57.6°C$. However, under sufficiently high pressure it shows the usual phenomenon of melting which it does at $-56°C$ at 5.2 atmospheres.

Liquefaction of Hydrogen and Helium— Hydrogen and helium have proved to be the most difficult to liquefy. Not only these have the lowest boiling points, their behaviour with regard to Joule-Thomson effect is anomalous too. Instead of the usual cooling effect they get heated when allowed to expand suddenly, and so could not be liquefied by the above method. It was later found that for each gas, at a particular pressure, there is a temperature called '*inversion temperature*', only below which the gas cools on expansion. For hydrogen the inversion temperature is $-80°C$ and for helium $-240°C$.

Hydrogen was liquefied independently by Travers (1901) and Olszewsky (1902) by applying Joule-Thomson effect after they had been initially cooled below their respective inversion temperatures. Hydrogen was obtained in large amount in liquid and solid form by Dewar. Helium was liquefied by Kammerling Onnes in 1908 by utilising similar principles and making use of liquid hydrogen for cooling. Helium was solidified by Keesom in 1926 in the Leyden Cryogenic Laboratory of Holland.

March towards the Absolute Zero— After solidification of helium the thrilling idea of reaching as close as possible to the unattainable absolute zero of temperature fired the imagination and engaged the attention of physicists. With the conventional

The different crystalline forms of the same substance are called *polymorphs*.

ALLOTROPY AND TRANSITION TEMPERATURE

The property possessed by an element to exist in different modifications giving rise to a difference in physical properties and to some extent chemical properties is called *allotropy*. The allotropes differ from one another in their energy content which may be due to an alteration of the number and arrangement of the atoms inside the molecules or in the arrangement of the atoms and molecules in the crystal lattice (framework). Three types of allotropy are distinguished depending on the method of transition from one modification to another ; (*a*) Enantiotropy. (*b*) Monotropy and (*c*) Dynamic allotropy.

(*a*) **Enantiotropy**—It is the form of allotropy where the two modifications are interconvertible at a definite temperature called transition temperature, one modification being stable above this temperature while the other form being stable below this temperature. (For Phase rule treatment, *vide* Ch. XV).

Example of this type is rhombic and monoclinic sulphur which has a transition temperature of 96·6°C. If sulphur is heated above this temperature it is slowly converted into the monoclinic form while below this temperature the rhombic variety is stable and the two forms can co-exist at this temperature. Another example is grey and white tin, the former crystallising in the cubic and the latter in the tetragonal system ; the transition temperature is 20°C below which the grey variety is stable while above this temperature the white one is the stabler. In very cold countries the usual white modification of tin becomes unstable and sometimes the rate of transformation from white to grey variety becomes so large that the whole falls to a powder with a cracking noise. This is called *tinplague*, or '*cracking of tin*'. It is reported that when Napoleon marched off from Russia in 1812, due to intense cold the conversion of white to grey tin became so rapid that tin buttons, medals and equipments of the soldiers crumbled away. So, the characteristics of enantiotropy are—

(i) *Existence of a transition temperature, and*

(ii) *Reversible interconversion of one form to another.*

(*b*) **Monotropy**— Systems in which one modification is constantly unstable at all temperature and gets converted into the stable variety, are called monotropic systems. So, here we can change one form into the other but can not effect the reverse change by temperature change only.

The system, ozone—oxygen, under ordinary circumstances, is an example of monotropy. At ordinary temperature, ozone is unstable and gradually decomposes into oxygen, the rate of decomposition rising with temperature. The system, red phosphorus—yellow phosphorus is another example for, in this case, if yellow phosphorus is heated for a long time it is ultimately converted into red phosphorus but the reverse change from red to yellow is not possible, unless the phosphorus is vaporised and recondensed. The explanation of this type of allotropy is that there is actually a transition temperature, which is well above the melting point. This explanation is supported by the fact that some systems which are

monotropic under ordinary conditions, become enantiotropic under increased pressure. So, the main characteristics of monotropy are—

(i) *The non-existence of any transition temperature, and*

(ii) *Uni-directional transition due to one form being constantly unstable.*

(c) **Dynamic Allotropy**—In this form of allotropy the two forms exist side by side in equilibrium at all temperatures, the proportion of the two forms present being determined by the temperature.

The most well-known example of this type is λ-sulphur and μ-sulphur which are both present in molten sulphur. Sulphur melts to an amber-coloured liquid which is almost wholly λ-sulphur containing a small percentage of μ-sulphur. As the temperature is raised the proportion of μ-sulphur increases and as a result of this the whole mass becomes viscous and dark in colour, until the boiling point is reached, where the whole mass is almost wholly μ-sulphur. So, the characteristics of dynamic allotropy are—

(i) *Non-existence of any transition temperature, and*

(ii) *Both forms co-existing at all temperatures.*

Methods of Determining Transition Temperature—Since the physical properties of the two modifications differ, it is to be expected that at the transition temperature any physical property will suffer a sudden change. This is the principle on which the usual methods of determining the transition point are based, the most widely used physical property for this purpose being the density or specific volume. This method is known as *dilato-metric* method. The substance is placed in a wide tube fitted with a capillary and sealed. The rest of the apparatus is filled with an indifferent liquid say, mercury, up to the capillary and the whole is placed in a bath whose temperature is gradually raised. The column of the capillary will rise uniformly with temperature up to the transition temperature where it will show a sudden change in volume due to the conversion from one form to another. When the conversion has been completed, the expansion will once again be uniform. The reverse phenomenon takes place on cooling.

Other physical properties used for the determination of transition temperature include solubility, electrical conductivity, vapour pressure, etc. The transition point between white tin and grey tin has been determined very ingeniously by observing the temperature at which grey and white tin have got the same electrode potential when dipped in a solution of a tin salt.

Comparison between Transition Point and Melting Point—In an extended sense the term transition point includes melting or boiling point, for, the latter is really a *reversible* transition or change from one state to another of the same substance. The following analogies are to be noted:—

(i) At the melting point or transition temperature both forms are equally stable having the same vapour pressure, and can co-exist side by side.

(ii) The transition point and melting point are perfectly well-defined temperatures, whose values are changeable with external pressure according to similar rules.

(iii) The transition from one modification to another as well as the melting takes place with either evolution or absorption of heat in the same way.

(iv) It is possible to superheat or supercool one modification above or below the transition point easily, but it is less easy to supercool a liquid below the melting point and far less easy to superheat a solid above the melting point.

(v) A dissolved foreign material depresses the M.P. and also changes the transition temperature according to the same basic rules.

SPECIFIC HEATS OF SOLIDS

Dulong and Petit's Law—Dulong and Petit (1819) discovered the very simple law that *the product of the atomic weight and the specific heat of solid elements is nearabout 6·4 i.e.*

Atomic weight × Specific heat = 6·4 (approx.)

This product of atomic weight and specific heat is called atomic heat and the law of Dulong and Petit is sometimes stated in the form that *atomic heats of all solid elements are constant and equal to 6·4*. This means that the thermal capacities of the atoms of all solid elements are the same. The following table shows the approximate constancy of the atomic heats. It is really striking that though the atomic weights extend from 7 to 238 yet the atomic heat values are nearly constant.

ATOMIC HEATS OF ELEMENTS

Element	Atomic weight	Specific heat	Atomic heat
Lithium	6·94	0·9408	6·53
Sodium	22·997	0·283	6·5
Aluminium	27·1	0·2142	5·81
Potassium	39·1	0·166	6·5
Copper	63·57	0·0928	5·83
Silver	107·88	0·0559	6·0
Iodine	126·9	0·0541	6·9
Gold	197·9	0·0304	6·25
Lead	207·2	0·0305	6·52
Uranium	238·5	0·0277	6·61

This law though empirically derived by its originators has been lent some theoretical support by Boltzmann who deduced it from the kinetic theory on the assumption that solid elements are composed of atoms executing vibration about their mean positions.

Exceptions to Dulong and Petit's Law— Some elements, *viz.*, carbon, boron, beryllium and silicon having low atomic weights and high melting points, are exceptions to the above rule, for,

their atomic heats at ordinary temperatures are 1·37, 2·64, 3·4 and 4·75 respectively, values much less than those demanded by Dulong and Petit's law. It has, however, been found that unlike other elements their atomic heats rise very rapidly with temperature and at higher temperatures approach the value 6. So, they are not really exceptions to Dulong and Petit's law, and the above fact suggests that the conditions under which an element obeys the above law are attained for these elements only at higher temperatures.

The variation of specific heat of elements with temperature at very low temperature is peculiar. At low temperatures, the specific heats of all elements decrease and almost approach zero. The explanation of this fact could only be satisfactorily given by Einstein on the basis of Planck's quantum theory. Later workers like Nernst, Lindemann, Debye and others developed the theory to such a high state of perfection that Jeans (1912) could write, "The application of quantum theory to the explanation of low temperature specific heats, from its complete naturalness, and from its agreement with experiment, seems destined to be final."

Molecular Heat : Kopp's Rule—The above idea was extended to the case of compounds by Neumann, Joule, Kopp, etc. who found that *the molecular heat of a solid compound (molecular weight × specific heat) is approximately equal to the sum of the atomic heats of the constituent atoms.* This is sometimes known as *Kopp's rule or Neumann's rule.*

The values of atomic heats which are to be used for metallic elements are nearabout 6·4 but, for non-metallic elements it is not so. The values are to be calculated either directly or from a determination of molecular heats of compounds and found to be less than 6·4. Thus, oxygen has an atomic heat of 4 cals., sulphur 5·4 cals, phosphorus 5·4, carbon 1·8, etc. It is interesting to note that abnormal values of atomic heats of elements like carbon, etc. are preserved even in combination. The above rule is only approximate and is, of course subject to the same limitations as that of its precursor, Dulong and Petit's law.

CRYSTAL STRUCTURE AND CHEMICAL CONSTITUTION

Mitscherlich's Law of Isomorphism— That the structure of a crystal is in some way related to its chemical composition was first recognised by Mitscherlich (1819) who stated this in his laws of isomorphism in the following way—*"The same number of atoms combined in the same manner produces the same crystalline form ; the crystalline form is independent of the chemical nature of the atoms and is determined solely by their number and mode of combination."*

Substances crystallising in the same crystalline form are called *isomorphous.* Examples of isomorphism among compounds of similar structure investigated by the discoverer of the law are the alkali metal phosphates and arsenates. Also, other

cases of isomorphism are well-known. Thus, common alum, ferric alum and chrome alum have similar structure $K_2SO_4,M_2(SO_4)_3,$ $24H_2O$ and are also isomorphous crystallising in the octahedral form. The sulphates of zinc, iron, etc. ($FeSO_4$, $7H_2O$, etc.) crystallise in the same crystalline form.

Criteria of Isomorphism—Only a similar outward crystalline form is not sufficient for two substances to be classed as isomorphous. The following are the three criteria of isomorphism.

    (a) *Similarity of crystalline form,*

    (b) *Formation of mixed crystals, and*

    (c) *Formation of overgrowth.*

(a) **Similarity of crystalline form**— This is the fundamental condition of isomorphism. However, in no system of crystal structure except the regular cubic system, perfect identity of crystalline form is ever met with. The interfacial angles between two crystals usually classed as isomorphous are never exactly equal, though they are very nearly so.

(b) **Formation of mixed crystals**— This is a very good criterion of isomorphism. If two substances which are isomorphous are crystallised from a solution containing both, it is found that the crystals which separate contain both the substances though the solution is saturated only with respect to one of them. If a solution containing violet chrome alum and ordinary potash alum is crystallised, it is possible to obtain crystals having a colour from deep violet to pale purple according to the amount of chrome alum present in the crystal.

(c) **Formation of overgrowth**—If a small crystal of one substance is suspended in a super-saturated solution of another substance, which is isomorphous with it, it is generally found that the crystal gradually grows in size. Thus, if a small violet crystal of chrome alum is suspended in a super-saturated solution of ordinary alum, the latter salt will be deposited as a colourless mass with the coloured crystal as nucleus, and thus a large crystal with a small coloured nucleus just like the plum in a plum cake will be obtained. In the same way a green crystal of nickel sulphate may be covered with an overgrowth of colourless zinc sulphate.

It seems that the property of formation of mixed crystal and overgrowth is in some way related to other properties of crystals, the most important of which is the molecular volume. For, it is sometimes found that isomorphous substances having widely different molecular volumes will not form mixed crystals or overgrowth, while substances which are not isomorphous but have almost equal molecular volumes may sometimes exhibit the above phenomena.

Application of the Law of Isomorphism —The law of isomorphism has served a great purpose in being helpful in the determination of atomic weight, for details of which the student is referred to Part VI.

Exceptions to the Law of Isomorphism—Though the law of isomorphism had quite well served its purpose in the earlier development of chemistry, yet further research has revealed the existence of many exceptions. The exceptions are two-fold. Firstly, there is the great difficulty of defining isomorphism. No two substances except those crystallising in the simple cubic system have been found which have exactly identical crystalline form: for example, ferrous sulphate and zinc sulphate, though crystallising in the same crystalline form, have their interfacial angles slightly different from each other. Another difficulty in the application of the law is brought out by the phenomenon of polymorphism *i.e.* the capacity of the same substance to crystallise in more than one form—a fact definitely against the fundamental postulates of the law of isomorphism.

Objections of a graver nature have been urged against the law of isomorphism. It has been shown that substances of quite different composition and number of atoms in the molecule may be isomorphous. Thus, silver sulphide (Ag_2S) and lead sulphide (PbS) are isomorphous as well as ammonium alum and alkali metal alums. Similarly exceptional is the isomorphous nature of calcium carbonate ($CaCO_3$) and sodium nitrate ($NaNO_3$) for, the chemical evidence is here sufficient to show that the two salts have a totally different structure. It has also been shown that substances having similar chemical structure may not be isomorphous.

It will be seen from the above discussion that the law of isomorphism is only an approximate generalisation which breaks down in quite a number of cases and therefore should hardly be called a law, but its importance lies in the fact that it had very ably rendered historic service in the most needful and crucial period of atomic weight determination.

X-RAY ANALYSIS OF CRYSTAL STRUCTURE

Classification of Crystals—The high order of symmetry and the serene beauty of crystals must have fascinated the philosophers and scientists alike from the earliest times, and extensive speculations were ventured about their structure. It was quite shrewdly and rightly guessed that there must be some inner regularity in the arrangement of the ultimate building blocks, and we owe to the geniuses of von Laue (1912), W. H. Bragg and W. L. Bragg (1913), P. Debye (1916) and others for a thorough elucidation of the problem with the help of X-rays.

From an examination of the external geometry of crystals, *viz.* the shape or interfacial angles, it has been found that all crystals can be classified under *seven systems* as shown in the table to follow. A crystal can be described with reference to three straight lines, not necessarily mutually perpendicular, and all the faces and interfacial angles can be expressed with the help of this *frame of reference*, a, b, and c standing for unit

5

lengths of the three axes of reference and α, β and γ for the angles between them.

System	Axes	Angles	Examples
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Rock salt, diamond, fluorspar, alums and garnet.
2. Tetragonal	$a = b$; c	,,	Tinstone, zircon and potassium ferro-cyanide.
3. Orthorhombic	a ; b ; c	,,	Rhombic sulphur, potassium nitrate and iodine.
4. Monoclinic	,,	$\alpha = \gamma = 90°$; $\beta \neq 90°$	Monoclinic sulphur, borax and sodium carbonate.
5. Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite, sodium nitrate and quartz.
6. Hexagonal	$a = b$; c	$\alpha = \beta = 90°$; $\gamma = 120°$	Beryl and graphite.
7. Triclinic	a ; b ; c	$\alpha \neq \beta \neq \gamma \neq 90°$	Copper sulphate and potassium dichromate.

From only the external form of a crystal it is not easy to judge to which crystal system it belongs. As for example, sodium chloride, which belongs to the cubic system and usually crystallises as cubes, may also crystallise as octahedra when allowed to
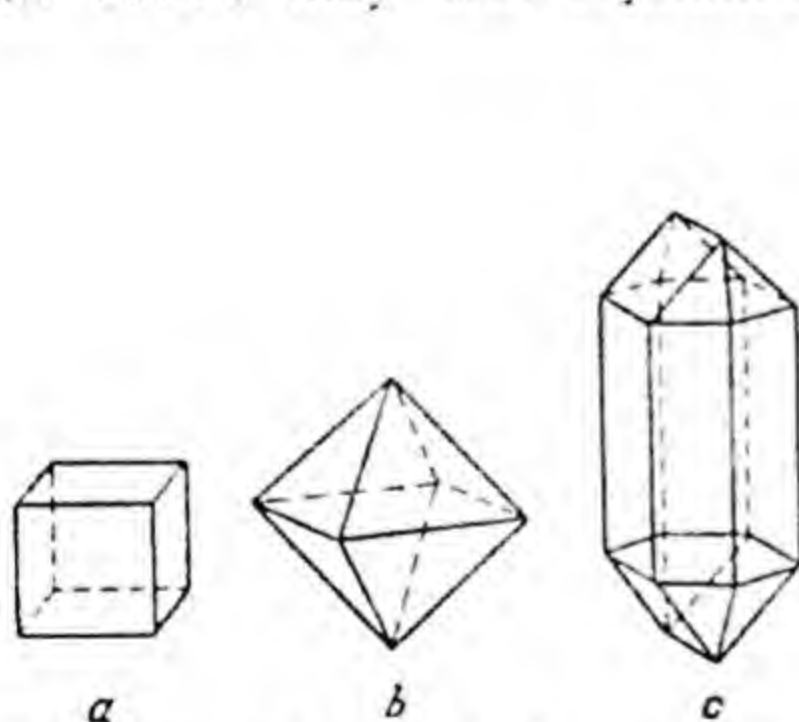

Fig. 24*a*—Cube, Octahedra and Prism
a, NaCl; b, alum; c, KNO₃
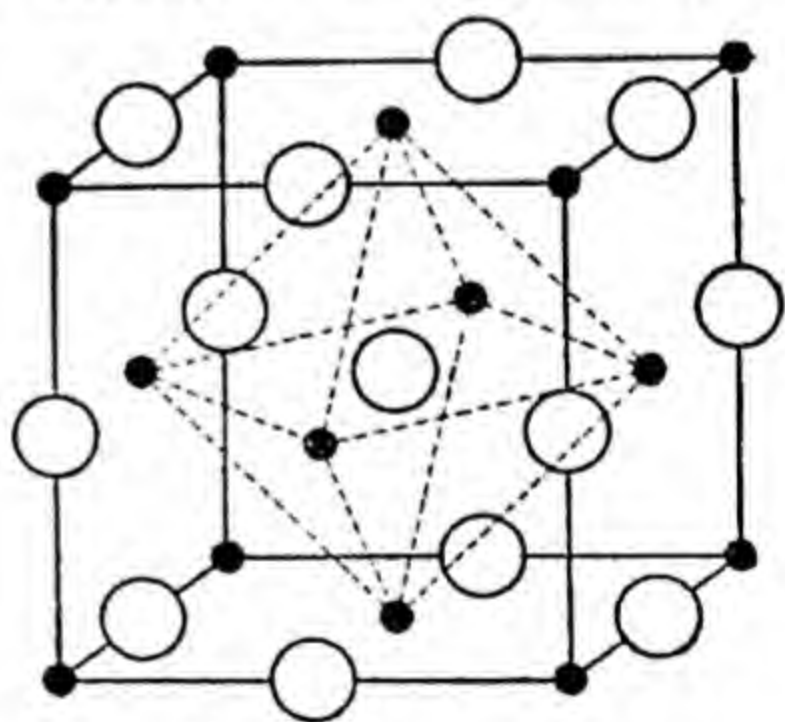
Fig. 24*b*—Same crystal as an
octahedron or a cube.

crystallise from urea solution. Both these forms belong to the cubic system, the octahedron being a cube with exclusive growth of the 111-faces (Fig. 24). The external appearance depends upon the mode of growth of the crystalline body, *i.e.* on crystal habit. Thus, if a crystal grows predominantly along one axis, it will appear as a needle whatever be the crystal system. So, the crystal system can be ascertained by a measurement of the interfacial angles and examination of the faces, and usually not by its geometrical shape.

Space Lattice and Unit Cell—For convenience of study, the inside of a crystal is visualised as an ordered assemblage of points in space, which are occupied by the crystal-building units. This regular array of points constitutes a three dimensional *space-lattice* (Fig. 25) and atoms and groups of atoms arranged on the space-lattice make the actual crystal. Axes of reference through any particular point are so chosen that they connect the nearest neighbours; and lines parallel to the axes are imagined to connect the array of points and thus the lattice is divided into small cubicles called *unit cells*. For cubic systems the unit cell is a cube. The atoms of the crystal are so arranged in the unit cell that the entire crystal body may be looked upon as its extension in space.
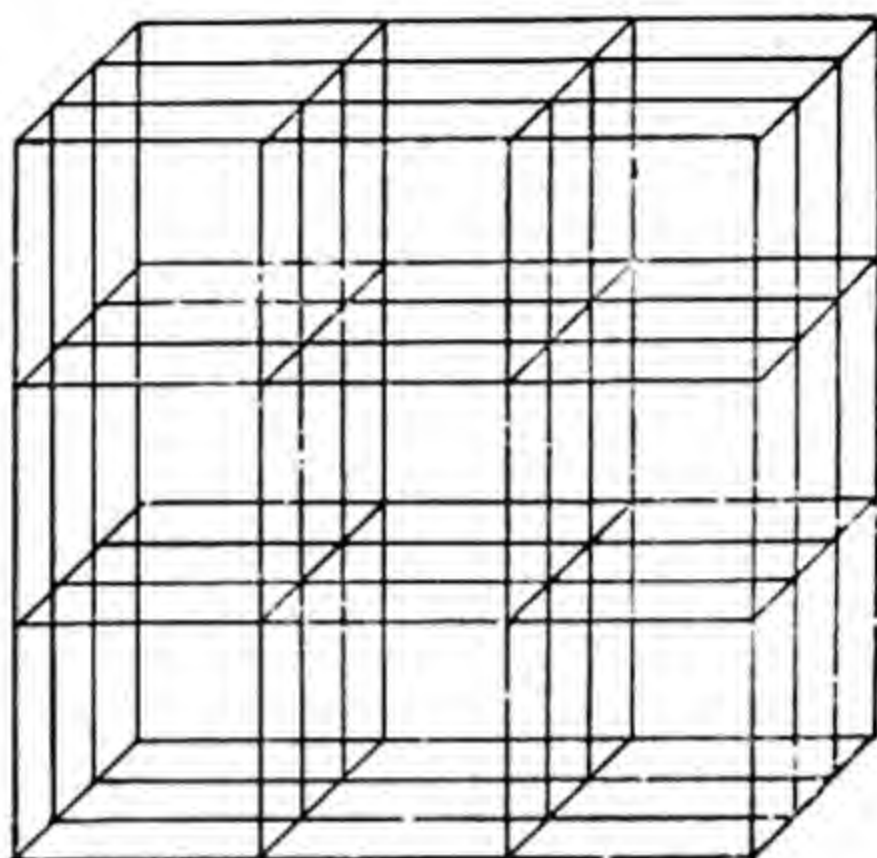

Fig. 25—Space Lattice

The Cubic System—Of all types of space lattices the easiest to visualise is the cubic system in which the axes are rectangular and of equal length (Fig. 26). Atoms can be arranged on this
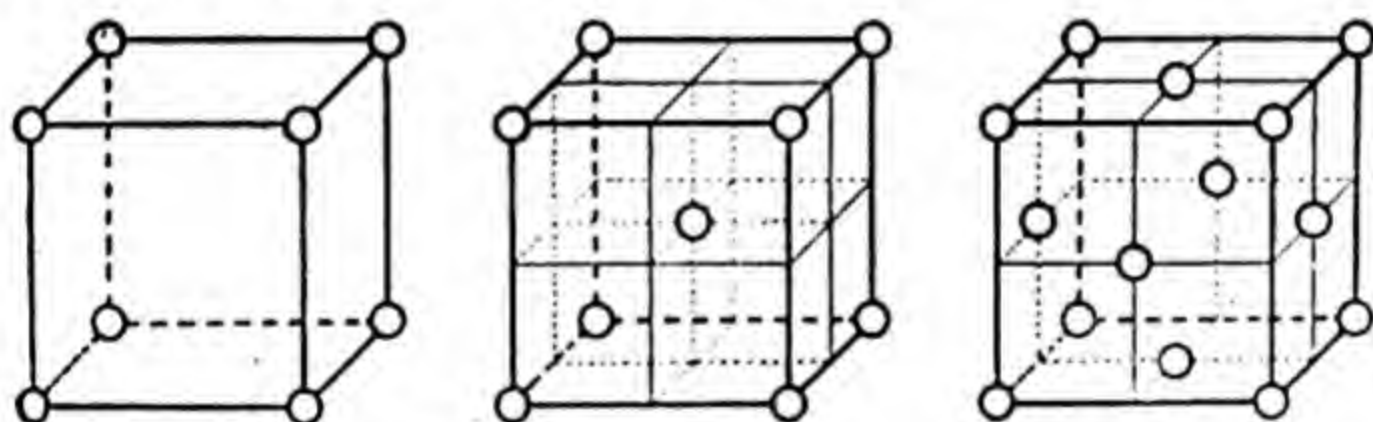
Fig. 26—Three types of Cubic Unit Cells.

three-dimensional frame-work in different ways and thus different types of cubic lattices are possible. Pure geometrical consideration limits the variation into three classes as shown in Fig. 26.

(*a*) The simple cubic lattice, where the units occupy only the eight corner points of the unit cube;

(*b*) The body-centred cubic lattice, in which each unit cube contains one building unit at the centre in addition to eight at the corners; and

(*c*) The face-centred cubic lattice with one unit at the centre of each of the six faces besides the eight of the simple cubic lattice.

Complicated lattices are formed by interpenetration of simpler lattices sometimes with some regularly recurring unoccupied lattice points. Thus the complex cubic lattice of diamond is formed by two face-centred systems.

100 PLANES   **110 PLANES**   **111 PLANES**
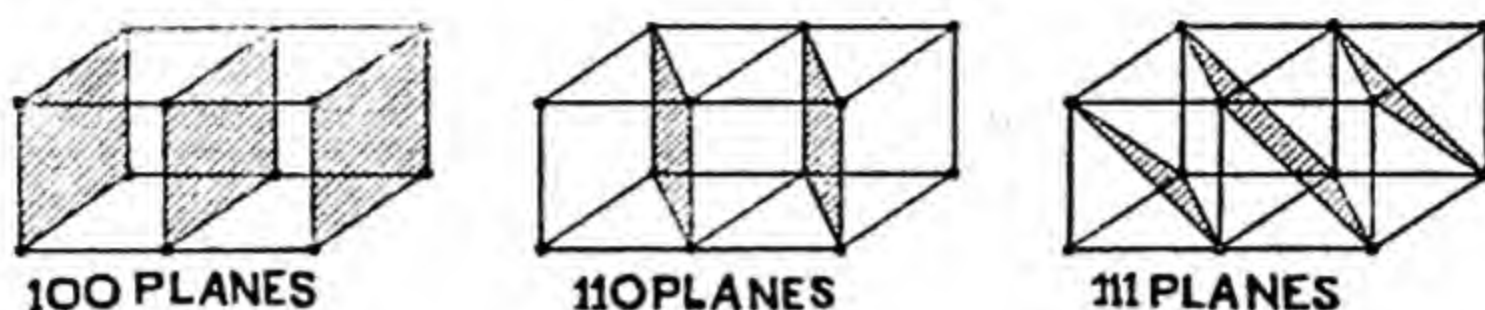
$$d_{100} = \sqrt{2}\, d_{110} = \sqrt{3}\, d_{111}$$

Fig. 27—Different faces of a Cubic Crystal

The various faces of a crystal of this type are designated by rational numbers which are reciprocals of the distances from the origin at which a given face intersects the three axes. Thus the number 111 (called one-one-one) denotes the face that cuts the three axes at unit distances (Fig. 27). Similarly, 110 is the name for the face that cuts the x- and y-axes at unit distances and runs parallel to the z-axis (Fig. 27) and 100 is the face which cuts x-axis at unit distance and is parallel to the other two axes.

Diffraction of X-rays by Crystals—When a beam of X-rays passes through a crystal, each atom in the path acts as a scattering centre and emits secondary radiation. At certain angles the scattered rays reinforce one another and at some they are destroyed by interference and thus give rise to the phenomenon of diffraction. From a study of the diffraction pattern it has been possible to get a picture of the inner architecture of a crystal.

This is embodied in the Bragg method which is graphically represented in Fig. 28. The incident X-ray wavefront, AB is reflected from successive layers. Let θ be the angle of incidence and the angle of reflection with respect to the reflecting plane.
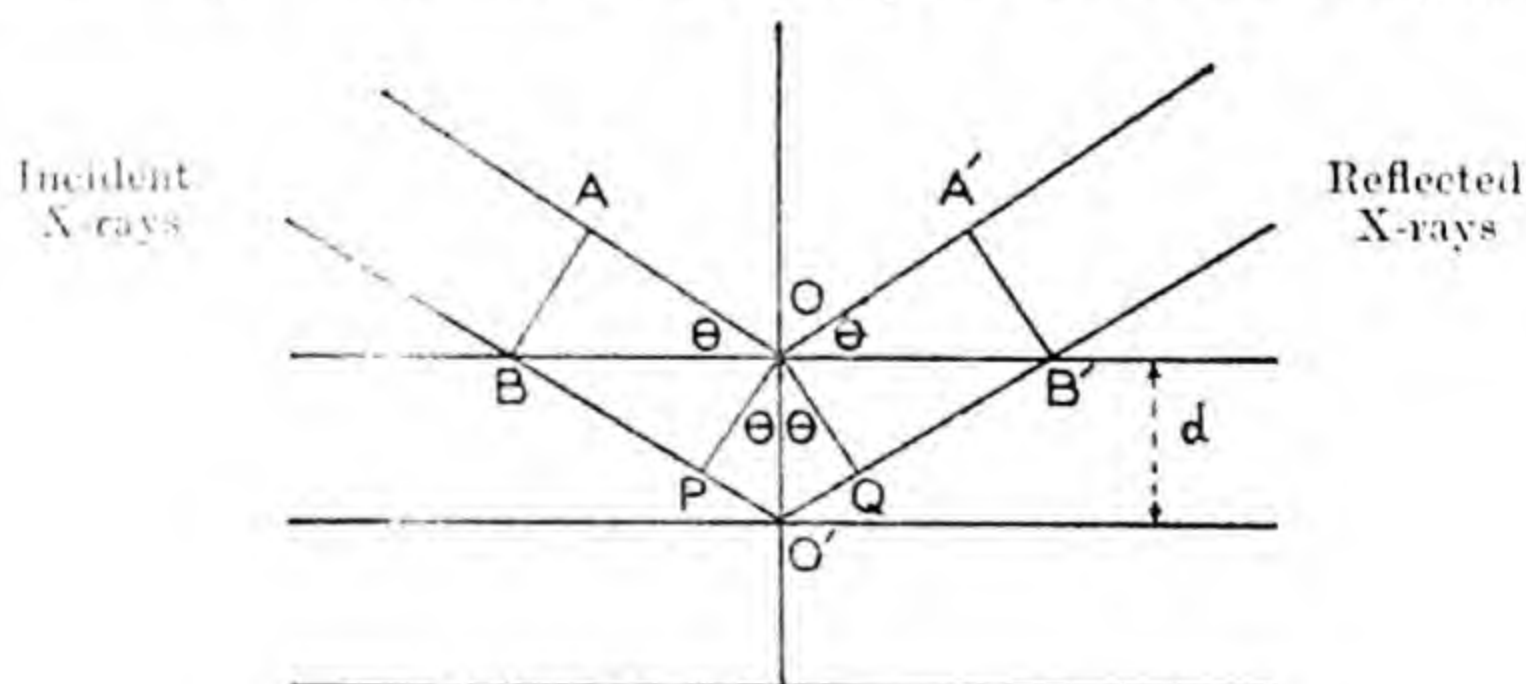

Fig. 28—Derivation of Bragg Equation

The beam reflected from the first layer, O A' and that reflected from the second layer, O' B' will reinforce each other when they

are in phase, *i.e.* when their path difference is an integral multiple of the wave length, λ. Now, the path difference is BO'B'—AOA' $= O'P + O'Q$ (OP and OQ being perpendiculars on O'B and O'B respectively)$= OO'$ Sin POO'$+ OO'$ Sin QOO'$= d$ Sin$\theta + d$ Sin$\theta = 2d$ Sinθ, d being the spacing of the layers. So the condition for the scattered rays to be in phase is

$$n\lambda = 2d \text{ Sin } \theta$$

which is the famous Bragg equation. In the equation n is any integer and its value is called the order of reflection.

Crystal Structure of Rock Salt (NaCl) by the Bragg Method (1913)—Determination of the structure of the rock salt crystal by W. H. Bragg is historically important in as much as it is the first success of the new X-ray method. The apparatus used by Bragg is shown in Fig. 29. It consists of a single crystal mounted at the centre of a revolving table. A monochromatic X-ray beam, produced on a rhodium target, is directed on the crystal and the reflected beam is received in an ionisation chamber connected to an electrometer. The deflection of the electrometer measures the intensity of the reflected beam.
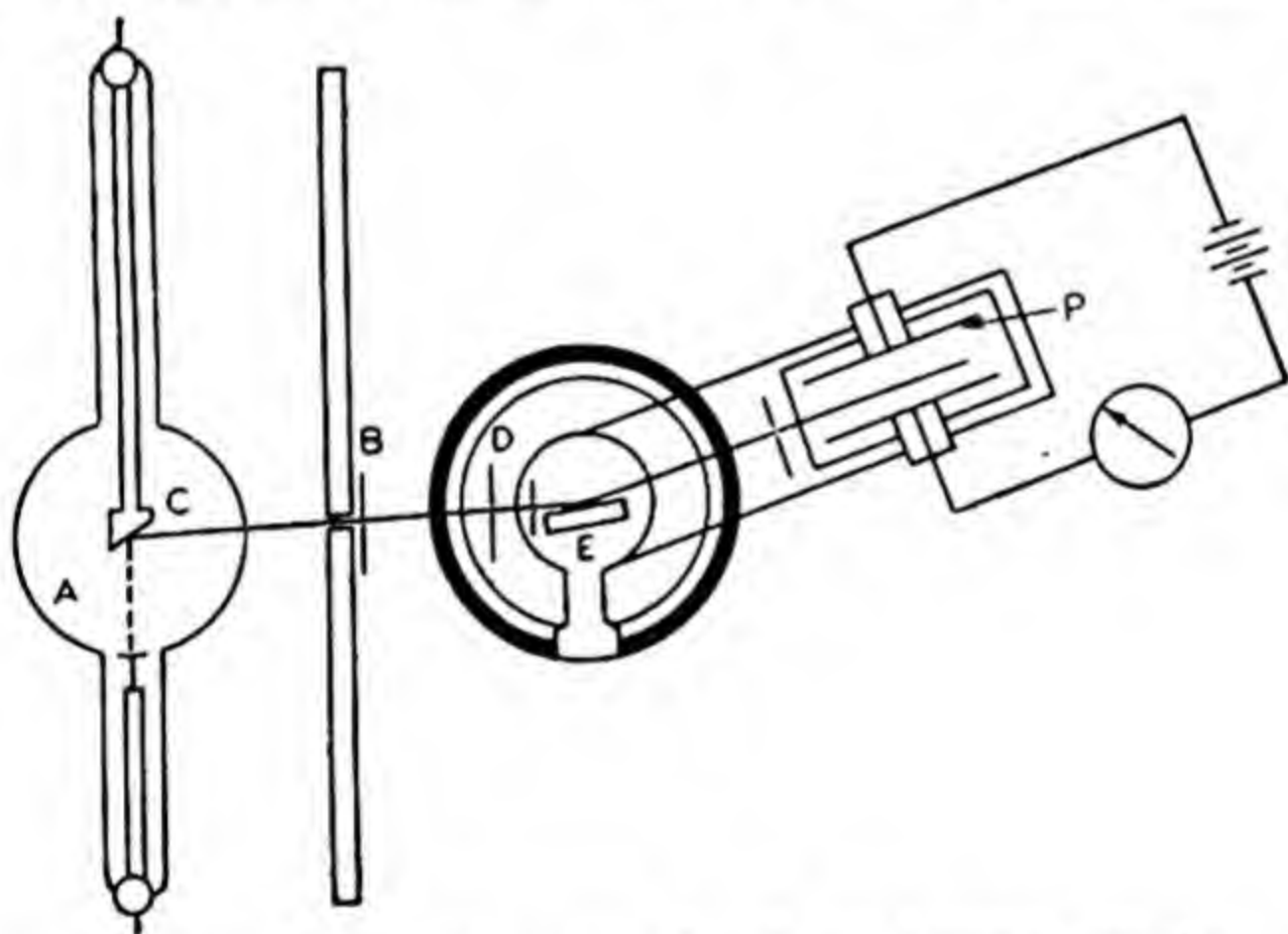
Fig. 29—Bragg Apparatus for X-ray Crystallography

Bragg rotated the crystal and measured the deflection of the electrometer for various angles of incidence of the X-rays. The results are shown in Fig. 30, where the intensity of a reflected beam, as measured by electrometer deflection, is plotted against the angle between the incident and the reflected beam, *i.e.* twice the angle of incidence. It is evident that as the crystal is rotated, for certain angles of incidence there is strong scattering, which evidently corresponds to the positions where the Bragg equation holds.

It is known that NaCl crystal is of the cubic system. For such crystals, if the interfacial spacing of the faces 100 be taken for unit, the spacings for 111 and 110 faces would be different

for simple, body-centred and face-centred cubic lattices. The
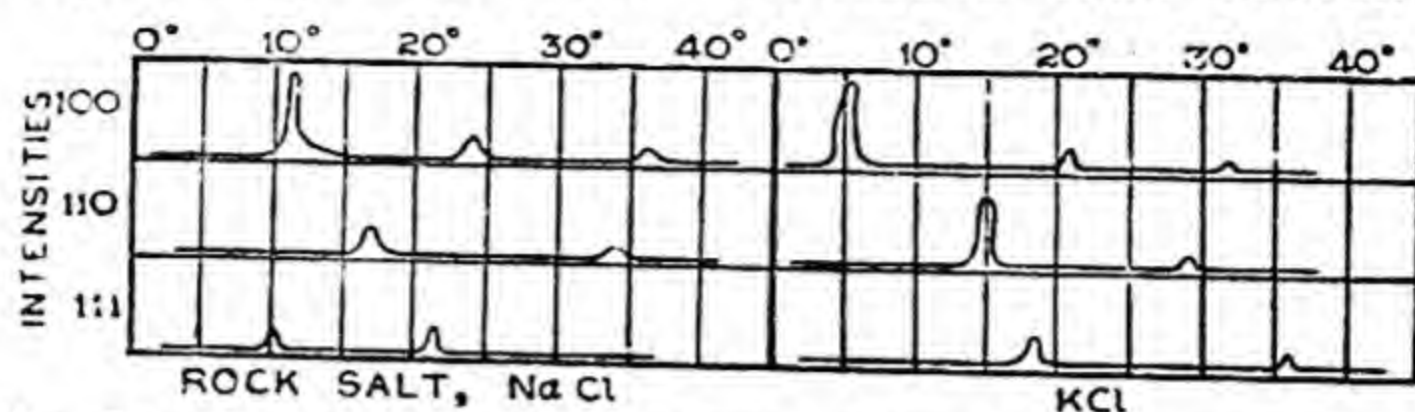
Fig. 30—Angular variation of Bragg Intensity for NaCl & KCl

respective values are given in the table below. In Bragg's experimental curves (Fig. 30) the first order maxima are found to appear at different angles of incidence for different faces, from which the relative interfacial spacings can be calculated for the

Type of Lattice	$\dfrac{d_{110}}{d_{100}}$	$\dfrac{d_{111}}{d_{100}}$
Simple cubic	·707	·577
Body-centred cubic	1·414	·577
Face-centred cubic	·707	1·154
Observed Values for ...		
Sodium Chloride	0·71	1·15
Potassium Chloride ...	0·71	0·58

different faces with the help of Bragg equation. These observed values are also given in the foregoing table. From a comparison of the calculated and experimental values given in the above table it is apparent that the rock salt crystal is a face-centred cubic one.

Fig. 31—Structure of Rock Salt as revealed by X-ray analysis.
[Actual (left), Cl⁻, bigger spheres; schematic (right)]

Another important point in Bragg's spectra is that for the 111-plane the first order reflection (*i.e.* for which $n=1$) is very weak and for the KCl crystal this is absent. These results are also in complete agreement with the structure of NaCl as shown in Fig. 31 which consists of a face-centred cubic array of Na^+ ions and another face-centred array of Cl^- ions, the two interpenetrating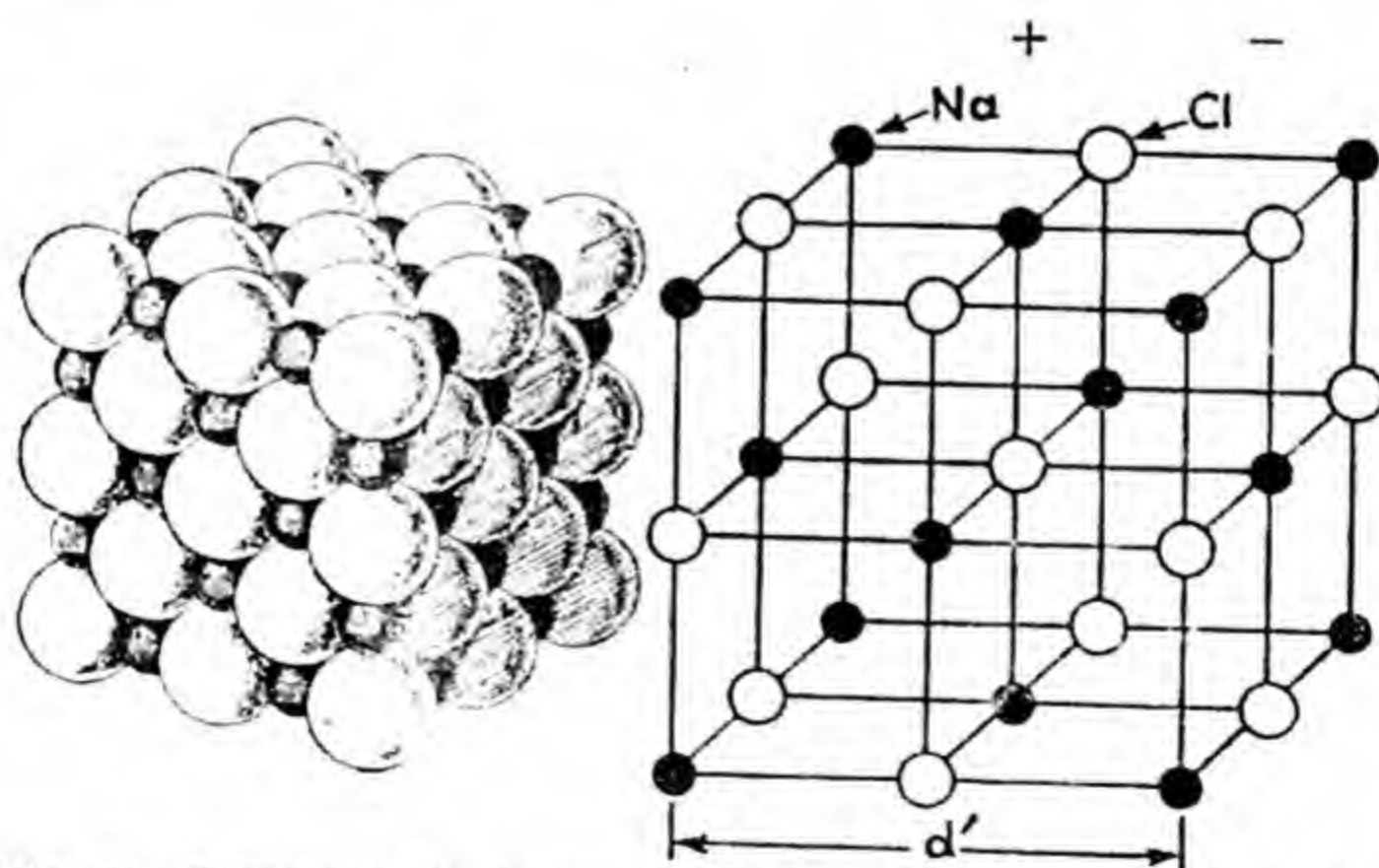 each other symmetrically so that each Na^+ is surrounded by six equidistant Cl^- ions and *vice-versa* (*co-ordination number six*). It is readily seen from Fig. 31 that the 100 and 110 planes contain equal numbers of Na^+ and Cl^- ions but the alternate 111 planes are built wholly of Na^+ ions or Cl^- ions. This creates the interesting situation that when the reflection for the 111 Na^+-planes are in phase, the reflection for 111 Cl^--planes are 90° out of phase with the Na^+-reflection and so the first order reflection is very weak in NaCl due to interference.

The scattering power of Na^+ ions is not exactly equal to that of Cl^- ions and so there is incomplete interference and a weak first order reflection is observed. However, in the case of KCl, the K^+ ion and the Cl^- ion being comparable in size and electronic structure, this interference is practically complete and the first order 111-reflection is absent, so that KCl appears as a simple cubic structure.

Once the NaCl structure was established, it became easy to extend the method to other crystals with confidence. Thus, KCl structure was investigated and found to be similar to that of sodium chloride but as explained in the previous paragraph, the scattering power of K^+ and Cl^- being about equal, it appears with X-rays to be simple cubic.

In the sodium chloride structure an atom of sodium has six chlorine atoms as its nearest neighbours and *vice versa*, and so the co-ordination number of these atoms in this structure is said to be six. In the closest packing possible, the maximum number of spheres which may be packed around a given one of the same size is twelve and many elements crystallise in this structure. Neon, argon, krypton and zenon are known to crystallise in this way consistent with the very small interatomic forces in these substances.

Some Applications of X-ray Crystallography— The above work of Bragg laid a sound foundation, and further refinements and improved methods have been developed. This has enlarged very much our knowledge about the structure of matter, and some simple typical structures are discussed below.

(*a*) **Diamond and Graphite**— Though both of them are elementary carbon, diamond is cubic whereas graphite crystallises in the hexagonal system.

In diamond every carbon atom is *tetrahedrally* linked to four other carbon atoms (co-ordination number four) at an internuclear distance of 1·54 Å, the same as the carbon—carbon distance in

aliphatic compounds. In fact, a diamond crystal may be regarded as a giant molecule (macromolecule), each carbon being linked by
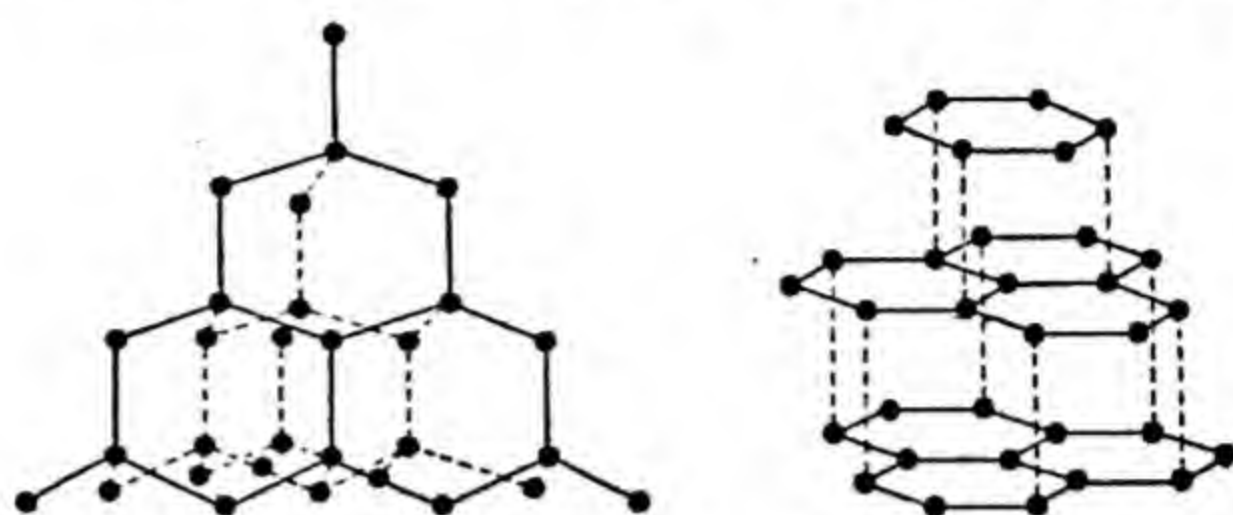

Fig. 32—Crystal structure of Diamond (*left*) and graphite (*right*).

covalent bonds to the neighbouring four carbon atoms. Such a structure is responsible for its extreme hardness and high melting point (Fig. 32).

Graphite on the other hand is a planar net-work of hexagons with C—C distance 1·42 Å, as in benzene. Each plane is separated from its next by a distance of 3·41 Å and so the interplanar forces are comparatively weak and this is responsible for easy cleavage of graphite.

The structure of diamond, for that matter for all crystals, is too idealised, and real crystals have lattice defects, which may consist of single or aggregate vacant sites or some interstitial atoms in the lattice. Such defects give rise to many interesting and useful properties.

(*b*) Alloys—X-ray analysis has given us a deep insight into the structure of alloys and inter-metallic compounds and has been of great importance in understanding their useful properties. For instance, Cu, Ag and Au are known to form alloys among themselves and with other metals. Up to a certain limiting composition these alloys are in a particular phase, called the α-phase, and with a further increase in the proportion of the second component a new phase called the β-phase, appears. X-ray analysis has revealed that throughout the α-phase the atoms of the second component simply replace those of the first in the hitherto existing simple cubic lattice. As the limiting composition is crossed, a body-centred lattice begins to be formed. Thus β-brass, represented by the formula CuZn, has a body-centred cubic lattice with Cu atoms occupying the centre of the cube formed by Zn atoms and *vice-versa*. In many alloys further phase changes are noticed and these have been found to be consequent on lattice changes. Generally, alloys become brittle on heating a ready explanation of which is that the crystalline order is disrupted by the increased thermal motion of the atoms.

Proteins, fibres and other long chain molecules, and also complicated organic molecules such as penicillin, vitamin B_{12}, etc.

have received intensive attention from X-ray crystallographers, which has helped to arrive at an understanding of their orderly internal arrangement.

Classification of Crystals according to Bond Types—The crystalline structure is due to chemical and quasi-chemical bonds existing between the building units, and depending upon the types of these bonds crystals can be classified into four general divisions.

(*a*) **Ionic Crystals,** in which the structural units are ions, bound together by strong Coulombic forces of attraction which supply most of the crystal energy. A typical example is the sodium chloride crystal. Due to the strong electrostatic binding forces such crystals are hard and have high melting points.

(*b*) **Metallic Crystals,** in which the metallic bond exists. Metals and alloys belong to this group. Only positive ions occupy the lattice points and a cloud of electrons pervades the space. As is characteristic of the metallic bond, the metallic crystals are highly conducting and opaque.

(*c*) **Covalent Crystals,** in which the building units are bound by primary bonds and as a matter of fact the entire crystal exists as one molecule. Diamond is an example. This structural peculiarity is responsible for its extreme hardness, high lattice energy and chemical inertness. Boron nitride (trade name : Borazon) obtained from two elements on either side of carbon in the periodic table has, as expected, a diamond-like lattice structure and hardness exceeding that of diamond.

(*d*) **Molecular Crystals,** in which van der Waals forces of attraction and, in extreme cases, hydrogen bonding between neutral molecules which usually are the building units in these crystals, supply the binding energy. Solid organic compounds come under this class. Due to comparatively weak binding strength these are low-melting.

Thus from the above discussions, one can perceive what a powerful tool has the X-ray technique been in unravelling the structural peculiarities of matter in diverse states of assemblage—from adamantine crystals to flexible rubbers ; and also in making it possible to have a pictorial representation of the location of the atoms and the space distribution of the electrons which bind them.

EXERCISE

1. What are the different kinds of allotropy? Explain with examples.

2. Write what you know of Dulong and Petit's law and discuss its merit as a method for the determination of atomic weights of elements. Give an account of the work which has been carried out in connection with the study of exceptions to this law.

3. Explain with illustrations what you understand by ;—(a) allotropy (b) isomorphous mixtures; (c) isomorphism.

4. What is Mitscherlich's law of isomorphism? State the uses to which it has been put. How would you definitely prove that the suspected case is one of isomorphism? Point out any apparent exceptions to the law.

5. Explain what is meant by "almost all the atomic weights can be determined through isomorphic relations."

6. Discuss the difference between allotropy and isomorphism.

7. Write notes on :—enantiotropy, monotropy, dynamic allotropy, transition temperature, space lattice and unit cell.

8. Discuss cubic system of crystal structure and describe how the structure of rock salt was determined with the help of X-rays.

CHAPTER VII

PHYSICAL PROPERTIES IN RELATION TO MOLECULAR STRUCTURE

Intensive and Extensive Properties— There are some properties of a system, called *intensive properties*, whose values are independent of the quantity of matter contained in the system, for example, temperature, refractive index, density, etc. Whether one considers one pound or ten pounds of a given system at uniform temperature, its refractive index is the same in both the cases and so, refractive index is an intensive property.

There are other properties, called *extensive properties* whose values are proportional to the mass of the portion of the system under consideration, for example, volume, internal energy, etc. The volume of ten pounds of matter is certainly ten times the volume of one pound of the same matter under identical conditions and so, volume is an extensive property. Any extensive property if expressed per mol or per gram basis becomes an intensive property. Most of the properties we shall study in this chapter are intensive properties.

Additive, Constitutive and Colligative Properties—Most physical properties per mol are partly *additive* and partly *constitutive i.e.* its total value per mol is the sum of the values which can be assigned to the constituent atoms in the molecule plus some corrections made for the chemical constitution or structure of the molecule. Physical chemists have bestowed a good deal of attention to find out the atomic values and the structural influences for various properties as we shall presently see.

There are some properties which are called *colligative* because they go together. This term is specially applied to vapour pressure lowering, osmotic pressure, freezing point depression and boiling point elevation as these properties for a solution are closely interrelated being directly dependent on the number of dissolved units in solution.

SPECIFIC AND MOLECULAR VOLUME

The volume in c.c. occupied by one gram of any substance is called its specific volume and the volume occupied by one gram molecule is called *molar volume*. So if the density be d and the molecular weight, M, we have,

$$Specific\ Volume = \frac{1}{d} \ and\ Molar\ Volume = \frac{M}{d} \ c.c./mol$$

Kopp (1842) was the first to undertake systematic investigations on the molar volumes of liquids. He measured the molar volume of liquids at their boiling points under atmospheric pressure and found that, in any homologous series, the molar

volumes of two successive members differed by a constant amount corresponding to the group CH_2 which pointed to the fact that perhaps every atom or group had a characteristic molar volume and in compound formation these values of their molar volumes were retained. He enunciated this as a law called **Kopp's law** which may be stated in the following way:—"*The molecular volume of a liquid is equal to the sum of the atomic volumes of the constituent atoms*".

The volume ascribed to one atom of any element is called its atomic volume and these values of atomic volumes are not the same as the true atomic volumes of the free elements. The atomic volumes of some common elements are $C = 11.0$: $H = 5.5$, O'' (in ketone, etc.) $= 12.2$: O'' (in acids) $= 11.0$; $>O$ (ethers) $= 7.8$ to 11.0 : $N = 15.6$: N (amines) $= 10.5$ to 12.0.

This law is only approximately true, the atomic volume of the same element changing markedly with its mode of combination. Also, according to Kopp's law, we would expect two isomers to have the same molar volumes, which is far from being true but generally speaking, the agreement among the values of two isomers as also that calculated from Kopp's law is within 5 per cent. So, the molar volume is not a strictly additive but rather a constitutive property.

SURFACE TENSION

The Nature of Surface Tension— The molecules of a liquid attract each other and the force of attraction falls off rapidly with the distance, and so it may be regarded that there is a sphere of attraction for each molecule which will attract other molecules if they fall within this sphere of attraction. A molecule which lies entirely inside the liquid is attracted equally from all sides, since its sphere of attraction lies wholly inside the liquid as a result of which there is no unbalanced force remaining on it. On the other hand, a molecule on the surface layer has got the liquid only on one side of it and so will be attracted by all the molecules in its sphere of influence towards the interior of the liquid. It is therefore acted upon by a force which tends to drag it in the interior of the liquid. This unbalanced force will gradually diminish with the depth and will vanish below a depth just equal to the radius of attraction of the molecules. So it appears that a thin layer on the surface is under a state of tension and work is to be done in bringing molecules from the interior to the surface i.e. in increasing the surface area.

Fig. 55—Molecular Attraction inside a Liquid.

The Definition of Surface Tension— Therefore, every liquid behaves as if it were enclosed by a skin or membrane, which always tends to contract so as to keep the liquid under tension. Imagine that a cut of 1 cm length is made in the surface membrane (the membrane of course does not exist, but the liquid behaves as if it does); there would be a force equal to the surface tension on each side of the line tending to open the slit. It is just like a sheet of rubber stretched across the top of a beaker. If a slit was to be made in the rubber, which was still kept under the same tension as before by some mechanical means, there would be a force on each side of the slit tending to open it; this force is the surface tension.

The surface tension therefore, is defined as the force in dynes along the surface acting at right angles to any imaginary line on the liquid. So its unit is dyne per cm. Note carefully that surface tension is not a pressure on the surface, but is a force along the surface acting at right angles to any imaginary line on the surface.

It is the existence of surface tension which imparts spherical shape to rain drops and causes capillary phenomenon. The magnitude of the surface tension depends on the nature of the liquid, on the nature of the vapour above it and on the temperature. The surface tension values *in dynes per cm.* of some well known liquids are given below.

Temp. °C	Water	Alcohol	Benzene	Acetone
0°C	75·64	24·05	31·58	26·21
20°C	72·75	22·27	28·88	23·70
40°C	69·56	20·60	26·26	21·16
80°C	62·61	...	21·26	16·2
100°C	58·85	15·47	18·78	...

Methods of Determining Surface Tension—Any phenomenon associated with surface tension affords a ready means for measuring its value. Thus, the weight of a drop falling from a capillary, the pressure inside a bubble in the liquid, etc., have been employed to calculate surface tension. But the most frequently used method is the determination of the rise of a liquid in a capillary tube, where the surface tension γ is given by the equation,

$$\gamma = \tfrac{1}{2} r h \rho g$$

ρ being the density, h the height of the liquid rising inside a capillary of radius, r and g, the acceleration due to gravity. For details, any text book on general physics should be consulted.

Variation of Surface Tension with Temperature—The surface tension of a liquid in contact with its vapour decreases with rise of temperature and becomes zero at the critical temperature.

Eötvös (1885) deduced theoretically that *molar surface energy,* $\gamma\left(\dfrac{M}{d}\right)^{\frac{2}{3}}$ of a liquid should be a linear function of temperature, where M is the molecular weight d, the density of the substance and γ, the surface tension. Later, Ramsay and Shields in 1893 experimentally verified the same and found that the following equation is valid for many liquids within a few degrees of the critical temperature.

$$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}} = K\ (T_c - T - 6) \qquad \text{(Ramsay and Shields' equation)}$$

where K is a constant, called Eötvös constant, which is approximately equal to 2.12 for many liquids and T_c, the critical temperature.

Application of Ramsay and Shields' Equation—This equation may be applied for various purposes : [*i*] firstly, it is possible to calculate the critical temperature from surface tension data, [*ii*] secondly, the molecular weight can be calculated from it and [*iii*] thirdly, the equation is employed to determine whether a liquid is associated or not, for it is believed that for all associated liquids, the value of the constant, K, differs from 2.12.

Molecular weight from Surface Tension— The calculation of molecular weight from the above equation is illustrated from the following data of Ramsay and Shields.

EXAMPLE—*The value of surface tension for benzene is 30.2 dynes per cm at 10°C and 28.2 at 25°C, the density of benzene at 10°C being 0.890 and at 25°C being 0.874.*

Take the general case where γ_1, and d_1, are the surface tension and density at temperature, T_1, and γ_2, and d_2 the corresponding values at T_2. So, $\gamma_1\left(\dfrac{M}{d_1}\right)^{\frac{2}{3}} = 2.12(T_c - T_1 - 6)$ and $\gamma_2\left(\dfrac{M}{d_2}\right)^{\frac{2}{3}}$

$= 2.12\ (T_c - T_2 - 6)$. Subtracting one equation from the other,

$$\gamma_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}} - \gamma_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}} = 2.12\ (T_2 - T_1)$$

Or $M^{\frac{2}{3}}\left\{ \gamma_1\left(\dfrac{1}{d_1}\right)^{\frac{2}{3}} - \gamma_2\left(\dfrac{1}{d_2}\right)^{\frac{2}{3}} \right\} = 2.12\ (T_2 - T_1)$

$$\text{or } M = \left\{ \frac{2.12\ (T_2 - T_1)}{\gamma_1\left(\dfrac{1}{d_1}\right)^{\frac{2}{3}} - \gamma_2\left(\dfrac{1}{d_2}\right)^{\frac{2}{3}}} \right\}^{\frac{3}{2}}$$

Substituting the values of T_1, T_2, d_1, d_2 and γ_1, γ_2 in the above equation we get 78.8 for molecular weight of benzene comparing very favourably against the theoretical value 78.

Parachor—The variation of surface tension with temperature can however be more accurately expressed by McLeod equation,

$$\gamma = k\,[D - d]^4$$

where D and d are the densities of the liquid and its vapour respectively, γ the surface tension and k, a constant called McLeod constant which is characteristic of the liquid and is independent of the temperature. If M is the molecular weight of the substance, the parachor P is defined by the equation,

$$P = Mk^{\frac{1}{4}} = \frac{M\gamma^{\frac{1}{4}}}{D-d}$$

i.e. the parachor is the fourth root of the McLeod constant multiplied by the molecular weight of the substance.

ATOMIC & STRUCTURAL PARACHORS

Atoms	Parachor	Structure	Parachor
Carbon	4·8	Double bond	23·2
Hydrogen	17·1	Triple bond	46·6
Oxygen	20·0	Semipolar bond	−1·6
Oxygen in esters	60·0	Benzene ring	6·1
Chlorine	53·8	Napthalene ring	12·2
Bromine	68·0	5-Membered ring	8·5
Nitrogen	12·5	8-Membered ring	2·4

If the density of the vapour, d is neglected in comparison with the density of the liquid the above equation can be written as

$$P = \frac{M\gamma^{1}/^{4}}{D} = \gamma^{1}/^{4}V_l$$

where V_l is the volume occupied by one mol of the liquid. If the temperature is such that the surface tension is unity, the parachor becomes equal to the molar volume and hence *the parachor may be regarded as the molar volume of a substance when its surface tension is unity.* Therefore, by comparing the parachors of various liquids, we are really comparing their molar volumes under unit surface tension.

Sugden showed that the parachor of a compound is an additive property and there are definite values associated with each atom depending on the particular way in which it is attached. Some of the values of parachors are recorded in the foregoing table. Since double bond, triple bond and coordinate covalent bond have definite values of parachor it is sometimes possible to differentiate between the possible structures by parachor measurement. As an illustration we can calculate the parachor of nitrobenzene. According to the classical view of pentavalency of nitrogen nitrobenzene has the structure, $C_6H_5N\!\!\underset{O}{\overset{O}{\diagdown}}$, whereas this is considered impossible by the Lewis theory of octet since this structure will necessitate ten

(five pairs) electrons round nitrogen. The alternative structure is $C_6H_5N\diagup^{O}_{\diagdown O}$, where the bond shown by the arrow is a coordinate covalent or semipolar bond formed only by one pair of electrons contributed by nitrogen. The calculated parachor for the first structure is 288·9 and for the second structure is 264·1. The observed value is 264·5 which admirably agrees with the second structure.

VISCOSITY OF LIQUIDS

The Concept of Viscosity—When a liquid flows, each portion of the liquid experiences a resistance to flow when flowing past another portion, somewhat similar to the friction between two solid surfaces. Viscosity of a liquid is a measure of this 'internal friction of a liquid'.

The idea can be easily grasped and quantitatively formulated from the simple picture of a liquid flowing in contact with a plane surface, P as shown in Fig. 34. The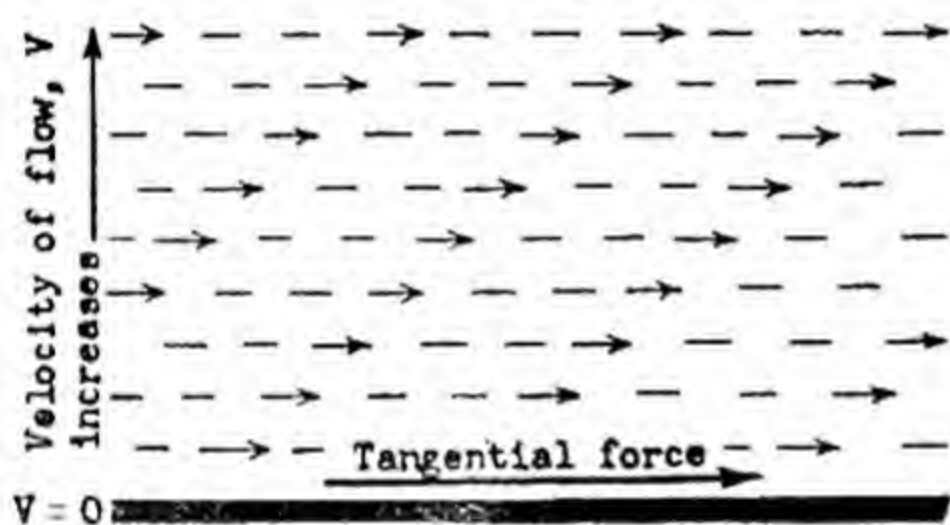re are two important points to be noted in this flow process. Firstly, the plane surface would experience a tangential force parallel to the direction of flow and would tend to move along the line of flow unless pegged down firmly. The second feature of this flow process is that there is a gradient of velocity of flow established at right angles to the direction of flow, in other words, the velocity of flow is zero on the stationary plane surface, P and increases continuously as we move up into the liquid at right angles to the direction of flow. Evidently, this tangential force on P depends on the area of the surface and on the velocity gradient. *This tangential force per unit area per unit velocity gradient is called the coefficient of viscosity of the liquid*, or simply, viscosity and is denoted by η. Evidently, viscosity governs the flow property of a liquid, the higher the viscosity the lower is its tendency to flow. The above concept of viscosity applies even when the stationary surface is absent, that is, in the interior of a flowing liquid and so viscosity is generally formulated as follows.

Fig. 34—Viscous drag on a fixed surface by a flowing liquid.

$$\text{Coefficient of Viscosity, } \eta = \frac{\text{Tangential force}}{\text{Area} \times \text{velocity gradient}}$$

Since the unit of force is dyne, that of area is square cm (cm²) and that of velocity gradient is cm per second per cm (Sec⁻¹), the

unit of viscosity is dyne-second per square cm. This unit is called a poise, after the name of Poiseuille, who first made systematic study of liquid flow through capillaries.

Experimental Determination of Viscosity —The most frequently used method of determining liquid viscosity is based on the determination of time of flow of a given volume of a liquid through a length of capillary tubing and to compare this time of flow with the time of flow of the same volume of another liquid of known viscosity. An apparatus in common use for this purpose is the Ostwald viscometer (also called viscosimeter), a form of which is shown in the diagram (Fig. 35).

A known volume of liquid is introduced in the viscometer maintained at constant temperature by immersion upto the neck in a thermostat. The liquid is pushed up by gentle blowing into the upper bulb and is allowed to flow under gravity to the lower bulb through the capillary. The time required for the liquid meniscus to pass between the two marks is determined with a stop watch. The time of flow is also determined for a liquid of known viscosity, say, water. If all the requisite precautions are taken, the viscosity is proportional to the product of time of flow and density, i.e. $\eta_1 : \eta_2 = t_1 d_1 : t_2 d_2$, and so the viscosity of the experimental liquid is easily computed.
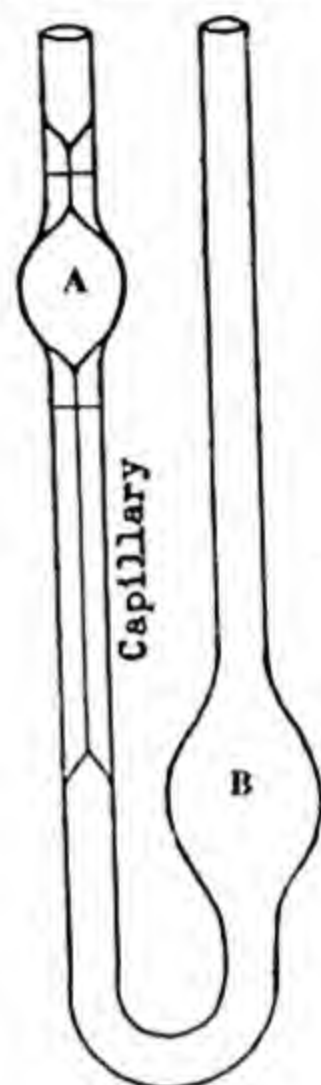
Fig. 35—
Ostwald
Viscometer

Viscosity Values and their Importance —Viscosity is an important determining factor in many properties concerning liquids, for example, the rate of fall of a solid through a liquid and also the rate of rise of a bubble through a liquid, the rate of flow of a liquid through an orifice or through a tube, any kind of movement of a solid inside a liquid and so on. Viscosity however affects only the rate and not the final position of equilibrium in any of these properties because in its definition there is a time factor involved, and so this property is called a rate property and such processes 'rate process' as opposed to equilibrium process.

The viscosity of ordinary liquids extends over a wide range, for example, from about two millipoise for ether to about ten poise for glycerine at nearabout room temperature. Water has a viscosity of about one centipoise near room temperature.

The viscosity of liquids generally decreases with rise of temperature, i.e. a liquid becomes more free-flowing at higher temperature. This is in sharp contrast with the behaviour of gases whose viscosity increases with rise of temperature. This indicates that the mechanism in the two cases is quite different. In gases it is a momentum transport phenomena caused by the kinetic motion of gas molecules from layer to layer, which has been likened

6

to the jumping of a group of people from one train to another to and fro between two trains in parallel unequal motion ; it is evident that such groups would resist the motion of the faster train relative to the slower one. Liquid viscosity on the other hand is due to intermolecular attraction or internal cohesion and so decreases with rise in temperature.

OPTICAL ROTATION

Specific and Molecular Rotation –Many substances, notably some organic bodies, have the peculiar property that if a plane polarised ray traverses such a medium, the plane of polarisation is turned through a certain angle. Such substances which rotate the plane of polarisation are called *optically active*. Those which turn the plane of polarisation to the right are called *dextro-rotatory* and those which turn the plane of polarisation to the left are called *laevo-rotatory*.

For purpose of comparison, the results are usually expressed in terms of specific rotation [α] for a fixed temperature and particular wave length (say, the sodium light), the specific rotatory power for a pure liquid being given by the equation.

$$[\alpha]^t{}_D = \frac{\alpha}{ld}$$

where $[\alpha]^t_D$ is the *specific rotatory power* at a temperature t°C and for the wave length of sodium D line. l being the length of the column of liquid in decimetres through which the light traverses and d is the density. For solutions, the concentration is substituted for density and the equation becomes.

$$[\alpha]^t{}_D = \frac{\alpha}{lc}$$

where c is the concentration of the solution in gms per c.c. The *molecular rotation* is obtained by multiplying the specific rotation with the molecular weight. Optical activity is usually measured by an instrument called the polarimeter, a full description of which is available in any text book of practical physical chemistry. Optical activity is often utilised for a rapid and accurate estimation of optically active compounds such as sugars, alkaloids and the like. For such purpose polarimeters are extensively employed in sugar factories.

Optical Activity and Chemical Constitution—That optical activity of organic compounds is due to some kind of asymmetry was vaguely pointed out by the great French chemist, Louis Pasteur, but the real credit of the discovery of the true cause goes to Van't Hoff and Le Bel (1874). Van't Hoff suggested that the four valencies of a carbon atom are directed towards the angular points of a *regular tetrahedron*, the carbon atom occupying the centre. If all the four groups are different the central carbon atom is called an *asymmetric carbon atom* and it

is easy to show by means of spatial models that there are two ways of arranging these four groups about the asymmetric carbon atom, giving two isomeric molecules which are mirror image to each other and cannot be brought into coincidence with each other. The two forms will be identical in chemical and physical properties except that one form will rotate the plane of polarisation to the right and the other to an equal degree to the left. In support of this theory it has been found that all organic compounds containing at least one asymmetric carbon atom can exist in both dextro and laevo-rotatory forms, but still now, there is no means of theoretically calculating the extent of rotation.

This type of optical activity arising out of molecular asymmetry, exists not only in carbon compounds but may also exist is almost all compounds of suitable structure containing multivalent (four or more valent) elements. Thus, optically active compounds of cobalt, platinum, silicon, tin, etc. have been prepared and studied.

Many transparent substances such as water, alcohols, etc. though not ordinarily optically active, can rotate the plane of polarisation if placed in a strong magnetic field, such rotation being called *magnetic rotation.* Perkin showed that this magnetic rotation is largely an additive property.

REFRACTION OF LIGHT

Specific Refraction—The refractive index of a liquid varies with temperature and in order to arrive at some measure of the refractive power of a liquid which is independent of temperature, Lorenz and Lorenz (1810) from purely theoretical reasoning arrived at the following expression for the *specific refraction constant, r,* and the molar refraction, $R=Mr$

$$r=\frac{\mu^2-1}{\mu^2+2}\cdot\frac{1}{d}\;;\;R=Mr=\frac{\mu^2-1}{\mu^2+2}\cdot\frac{M}{d}$$

where μ is the refractive index and d is the density.

SPECIFIC REFRACTION CONSTANT OF LIQUIDS (C.C.)

Substance	$\frac{\mu-1}{d}$		$\frac{\mu^2-1}{\mu^2+2}\cdot\frac{1}{d}$	
	Liquid	*Gaseous*	*Liquid*	*Gaseous*
Water	0·3101	0·3334	0·2068	0·2068
CS₂	0·4347	0·4977	0·2398	0·2405
CHCl₃	0·2694	0·3000	0·1796	0·1790

The value of r arrived at from this formula holds constant for a fairly wide range of temperature and is equally valid for the liquid and the gaseous state. The foregoing table, quoted from the work of Brühl, illustrates the above points, the wave length used being that of the D line for sodium.

Atomic and Molecular Refractivity—The product of the specific refraction and atomic weight is called *atomic refraction* and the product of the specific refraction and molecular weight is called *molecular refraction*, R, which is given by the formula shown above, where M is the molecular weight of the substance.

Brühl showed that molecular refractivity is to some extent an additive and to some extent a constitutive property. Thus an atom, say, of carbon has got different values of its atomic refraction depending on its mode of linkage. The atomic refractions of some common elements are as follows:

Hydrogen, (H).........1·051 ; Hydroxyl oxygen, (O).........1·21 ; ethereal oxygen, (O)......1·683 ; Ketonic oxygen, (O)"......2·287 ; double bond,......1·709 ; chlorine, (Cl)......5·998, etc.

Given the molecular formula and the structure of a compound, the molar refractivity can be calculated from such a table and compared with the observed value. Brühl has sometimes applied this method for gaining information as to the existence of certain types of bonds, but after all, the evidence will be accepted with caution as the additivity of molecular refractions is only approximate.

ABSORPTION OF LIGHT

General Description—If a ray of light is passed through any transparent medium, a portion of the light may be absorbed. The amount of absorption depends, among other factors, on the nature of the medium and on the wave length of the light passing through the medium. For example, a colored solution absorbs visible light and, in fact, that is why it is called colored. On the other hand, benzene, which has no absorption in the visible and so is colourless, absorbs strongly in the near-ultraviolet. Had human eyes been sensitive to this region of the spectrum, benzene would have appeared intensely colored.

The absorption spectra of gases and vapours consist of a large number of discrete lines and bands and have been thoroughly investigated by spectroscopists. It is, however, beyond the scope of the present work to give even a brief account of this field and only a very elementary treatment will be given later in Part V. The absorption spectra of liquids, however, contain broad lines or regions, and intensive studies have been made of absorption of light of ultraviolet, visible and infra-red regions with various liquids and solutions. The apparatus, generally employed in these investigations, is called a *spectrophotometer* which measures the intensity of light of different wave-lengths before and after passing through a given liquid. Simpler devices like *colorimeters* or *absorptiometers* are also used for the same purposes.

Mechanism of Light absorption —The ultraviolet (U.V.) and visible portion of the spectrum which is ordinarily investigated for analytical and other purposes extends from 200 m μ (milli-

micron) to about 400 m μ for the ultraviolet and from about 400 m μ onward to somewhat below 800 m μ for the visible. The mechanism of light absorption in these regions is similar and is essentially electronic in origin. The absorption of light is caused in these regions by the energy of the radiation being transferred to electrons in the outer orbit of the molecule, which undergo transition to higher energy level. Absorption in the infra-red (I.R.) on the other hand, does not involve any electronic transition but is governed by oscillation and displacement of the atoms in the molecule, and hence I.R. spectrum is often called vibrational and rotational spectrum. Besides this fundamental difference in theoretical approach, the experimental technique for I.R. is somewhat different and difficult, and so I.R. absorption is treated separately from visible and ultraviolet absorption.

Applications of Light Absorption Measurement—In physical chemistry the most important applications of measurement of light absorption of liquids are (a) for rapid chemical analysis of a mixture, a component of which has strong absorption at a convenient wave-length and (b) for the determination of chemical structure of organic compounds.

(a) **Analysis by Light Absorption**—The principle of such analyses is very simple. Suppose we know the intensity of light absorption at a suitable wave-length of a colored substance, say methylene blue, at various concentrations; it is now very easy to estimate methylene blue in a similar solution of unknown strength by measuring its absorption at the same wave-length.

It should be noted that absorption is not proportional to concentration, i.e. doubling the concentration does not bring about double absorption. It rather follows an exponential law with respect to concentration or thickness through which light passes. In other words, if a certain concentration cuts off a certain fraction of incoming light, every equal increment in concentration would bring about a further reduction by the same fraction. This is expressed mathematically by the Beer-Lambert Law,

$$I = I_0 e^{-\epsilon cd}$$

where I_0 is the original intensity, I is the intensity after absorption by a solution of concentration c and thickness d, and ϵ is a constant called the absorption coefficient or index. So measuring the ratio, I/I_0 and knowing ϵ from previous determinations it is easy to calculate c, the concentration of the dissolved substance. This principle is extensively used in colorimetric estimation.

(b) **Absorption Spectra and Chemical Constitution**—The absorption spectrum of a compound is closely related to its constitution. Hantz, Hartley and others have used the method to investigate the tautomeric nature of certain organic substances by comparative methods based upon the generalisation that substances of similar constitution have got the same type of absorp-

tion spectra; for example, all the permanganates have got similar absorption spectra, and so on.

As an application of this method, a case cited by Hartley will be described. The constitution of isatin, an oxidation product of indigo, could be represented according to its chemical properties either as formula I or as formula II.

I. $C_6H_4\underset{NH}{\overset{CO}{<}}>CO.$ II. $C_6H_4\underset{N}{\overset{CO}{<}}>COH$

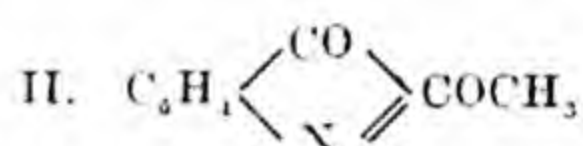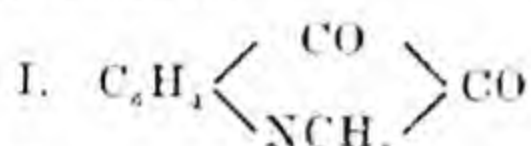(Lactam Structure)   (Lactim Structure)
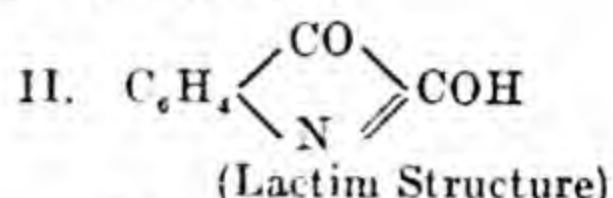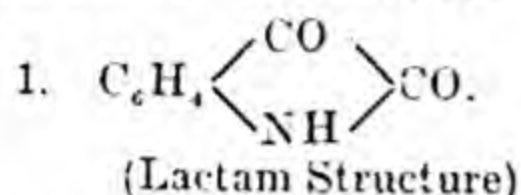
Two isomeric methyl derivatives of isatin are known and their constitutions are known with certainty. They have the following two structures.

I. $C_6H_4\underset{NCH_3}{\overset{CO}{<}}>CO$ II. $C_6H_4\underset{N}{\overset{CO}{<}}>COCH_3$

The absorption spectrum of the second methyl derivative was found to resemble very closely that of isatin and so it is argued that isatin has the formula II i.e. has lactim structure.

However, this method, as far as visible and ultraviolet spectra are concerned, has been found to give unreliable information in many cases and has lately fallen into disrepute. Infra-red spectra, on the other hand has been found to be more reliable and at present extensive use is made of infra-red absorption in identification and determination of structure of organic compounds.

(c) **Infra-red Absorption**—No single tool has had a more dramatic impact on the *modus operandi* of organic chemists than the instruments for infra-red measurements recently commercially developed to a state of perfection suitable for routine laboratory use. Undoubtedly this is due to the simple and unambiguous interpretation of I.R. absorption data correlating them with the presence of functional groups in an organic molecule, so much so, that I.R. absorption curves are often called the "finger prints" of organic molecules, and are extensively used for identification of organic molecules as a routine laboratory procedure.

Absorption in the infra-red is linked with rotation and vibration of atoms or groups of atoms in a molecule and, unlike absorption in the visible and ultra-violet, does not involve any electronic excitation. Consequently, the infra-red absorption is very characteristic of the structure of a molecule. In fact, it is possible to correlate infra-red absorption in a certain region with certain chemical groups; for example, the $C=O$ group has an absorption peak at about 1.70μ (micron) the -OH group near 3.10μ and so on, and these absorption peaks are only slightly shifted by the presence of other groups in the molecule. Hence, the presence of certain groups in a complicated organic molecule can be identified with a fair degree of certainty by a study of its infra-red absorption spectrum (called I.R. absorption). I.R. absorption of organic compounds can be measured either in the dissolved state or in

suspension. The method is so dependable for identification purposes that it has nowadays become a routine method in synthetic organic chemistry, specially, to prove the presence or absence of functional groups in an unknown molecule.

X-ray analysis is also nowadays used for determination of structure of organic molecules. It is possible with the help of X-ray crystal analysis to make electron density distribution maps of suitable organic molecules. Two recent facts of great interest are that in the case of penicillin and Vitamin B_{12}, such maps were made before the complete structure was established by the organic chemists. In fact, these X-ray maps established decisively the chemical structures of these complicated molecules, so that organic chemists could attempt their synthesis on a sure knowledge of their structure.

ELECTRICAL PROPERTY

Dipole Moment—When a substance is placed in an electric field, say, between the plates of a charged condenser, the molecules experience a kind of electrical stress which tends to separate the positive charge from the negative charge inside the molecule. In other words though normally the centre of positive charge in the molecule might coincide with the centre of negative charge in the molecule, under this electrical field the molecule would show a separation of charge.

Whenever two equivalent amounts of positive and negative electricity are separated by a distance they are said to form a dipole and according to standard derivation in electrostatics such a dipole has a dipole moment, el where e is the value of each of the charges which are separated by a distance, l. Hence, the applied electric field has *polarised* the molecule which has now a definite *induced* dipole moment.

Origin of Dipole Moment—So far we have regarded that the molecule normally has no dipole moment which latter is induced in the molecule only under the influence of the electric field. It is however, possible that some molecules have already an electric dipole moment inherent in their structure. Let us consider the case of the molecule HCl. We know that there is a pair of electrons which binds the hydrogen and chlorine by a covalent bond. However this electron pair is not exactly at the middle of the molecule but will be drawn closer to chlorine than to hydrogen, since chlorine is more electronegative (electron-attracting) than hydrogen. This will cause the hydrochloric acid molecule to have a *permanent* dipole moment in addition to that to be induced by an external electric field. This kind of permanent polarization is called orientation polarisation of the molecule and the associated *permanent* electrical moment is called the dipole moment, μ of the molecule.

Dipole Moment and Molecular Structure—There are various methods of determining dipole moments which however

will not be given here. The following table contains data on dipole moments for a few compounds. Compounds which have zero or almost zero dipole moments are called nonpolar com-

DIPOLE MOMENTS

Inorganic Compounds			
H_2, N_2, Cl_2, Br_2, CO_2, CS_2, $SnCl_4$	0	H_2S	1·10D
HCl	1·03D	CO	0·10
HBr	0·78	NH_3	1·46
HI	0·38	SO_2	1·6
H_2O	1·84	PH_3	0·56
		H_2O_2	2·1
Organic Compounds			
Methane, ethane,	0	alcohols	1·7 D
Ethylene, acetylene	,,	ethers	1·15
Carbon tetrachloride	,,	ketones	2·7
Benzene, napthalene	,,	chlorobenzene	1·73
Methyl chloride	1·86D	nitrobenzene	4·23
Methyl bromide	1·78	benzonitrile	4·37

pounds, whereas compounds with appreciable dipole moments are called *polar compounds.*

It will be observed that compounds like carbon disulfide or carbon dioxide or carbon tetrachloride which we know from considerations about the symmetry of the molecule or the electronegativity of the constituent atoms to be non-polar, have zero dipole moments. It should also be noted that the dipole moment of water is not zero, which shows that the three atoms are not in one line. In fact, it has been shown by other physical methods that the three atoms in a water molecule are arranged on the corners of a triangle, the OH bonds forming with each other an angle of about 110°. Similar remarks also apply to H_2S. Also, NH_3 molecule has a high dipole moment showing that it is not a triangular structure with the nitrogen at the centre in one plane but actually it has almost a tetrahedron-like structure, nitrogen being at the centre, the hydrogen atoms occupying three corners and the fourth corner being vacant.

Fig. 36—The shape CS₂, CO₂ and H₂O molecule

Note that the dipole moments are given in Debye units (D), which is 10^{-18} electrostatic unit. This is the right order of magnitude because the electronic charge is of the order 10^{-10} electrostatic unit and the inter-atomic distances are of the order of 10^{-8} cm; therefore, the moment which is their product will be of the order of a Debye unit.

THERMAL PROPERTIES

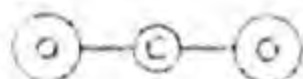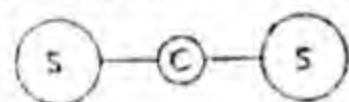**Heat of Vaporization and Trouton's Rule**— Trouton pointed out an interesting relationship between heat of vaporization

and boiling point. This relationship is generally known as Trouton's rule and is expressed as

$$\frac{L}{T_b} = 21$$

where T_b is the boiling point of the liquid in the absolute scale and L the molar heat of vaporization. In other words, the molar heat of vaporization of a liquid is directly proportional to its absolute boiling point. We shall see later in the chapter on thermodynamics that heat absorbed reversibly divided by temperature is to be called *entropy*, and so the thermodynamic interpretation of Trouton's rule is that *the entropy of evaporation of all liquids is nearly the same.*

This relationship holds fairly well with unassociated liquids but does not hold good with associated liquids like water, alcohols, acids, etc., as will be seen from the following table. This rule can be deduced thermodynamically from Clausius-Clapeyron equation with some assumptions.

TROUTON'S RULE FOR LIQUIDS

Liquids	Molar Latent Heat, L.	Boiling Point, T_b	Trouton Constant, L/T_b
Helium	22	4·2°K	5·2
Hydrogen	216	20·4	10·6
Oxygen	1,630	90·1	18·0
Methane	1,951	108	18·0
Hexane	6,996	342	20·0
Carbon tetrachloride	7,140	350	20·4
Benzene	7,497	353	21·2
Acetone	7,238	330	21·9
Water	9,700	373	26·0
Ethyl Alcohol	9,448	351	26·9
Ethylene Glycol	11,760	470	25·1
Acetic Acid	5,787	391	14·8

Boiling Point and Critical Temperature—In this connection it is of interest to observe that the boiling points of all liquids are approximately two-thirds of their critical temperature, both temperatures being expressed in the absolute scale. In other words, all liquids at the boiling point are at nearly corresponding temperatures. This was first observed by Guldberg (1910) and is sometimes referred to as *Guldberg rule*. This relation is only approximately true as the observed value of T_b/T_c is found to lie within the range 0·60 to 0·70 instead of being equal of 0·67 (= 2/3). Some typical values are collected in the following table.

BOILING POINT AND CRITICAL TEMPERATURE (*Guldberg Rule*)

Substance	Boiling Point, °K	Critical Temp. °K	T_b/T_c
Hydrogen	20·4	33·2	0·614
Oxygen	90	154·3	0·583
SO$_2$	263	430·2	0·611
H$_2$O	373	647·3	0·576
Benzene	353	561	0·629
Octane	398·5	569·2	0·70
Decane	446	603	0·74
Ether	308	467	0·661
Methyl alcohol	339	513	0·662
Octyl alcohol	468·5	658·5	0·712

EXERCISES

1. Write short notes on—(*a*) colligative property, (*b*) asymmetric carbon atom, (*c*) Kopp's Law, (*d*) parachor.

2. How is molecular weight determined from surface tension data.

3. Define the following—(*a*) specific refraction, (*b*) specific rotation, and (*c*) atomic refraction.

4. How is the absorption spectrum of a substance utilised in determining its chemical constitution.

5. Explain and illustrate the following :—Non-polar molecules, polar molecules, dipole moment and orientation polarisation. What is the usual unit of dipole moment and indicate how this unit is theoretically derived.

6. What are intensive and extensive properties. Discuss the same with reference to the following properties, *viz.*, viscosity, surface tension, surface energy, pressure, volume, and dipole moment.

7. What are colligative properties?

8. Write down the units of all the properties you have studied in this chapter and their numerical values for water.

PART II

THERMODYNAMICS AND PHYSICOCHEMICAL EQUILIBRIA

FIRST Law of Thermodynamics—Thermochemistry—Second Law of Thermodynamics—Solutions: General—Physical Chemistry of Dilute Solutions I. Osmotic Pressure—II. Lowering of Vapour pressure and Related Properties—Equilibria in Homogeneous Systems—Equilibria in Heterogeneous Systems. Phase Rule.

CHAPTER VIII

FIRST LAW OF THERMODYNAMICS

The Scope of Thermodynamics— Almost all processes in nature are accompanied by energy changes. This energy manifests itself in various forms e.g. mechanical, electrical, heat, radiation, etc. These different forms of energy are interconvertible under suitable conditions and of all the forms of energy, heat energy occupies a unique position as all other forms of energy tend to be ultimately converted into heat.

The science of thermodynamics attempts to study the laws underlying the interconvertibility of the different forms of energy into heat and to find out the relationships between the different properties of matter which are deducible from these laws. The laws of thermodynamics are based on human experience about the behaviour of *macroscopic* systems, i.e., comparatively large systems which are an assemblage of a large number of molecules, and hence, these laws hold good quite rigidly. Since human experience is limited to grossly palpable quantities of matter which are far from being anything on a molecular scale, the deductions of thermodynamics are independent of any hypothesis about the molecular structure of matter. Further, the science of thermodynamics does not concern itself with the time element in any transformation and hence it has no valid application in the study of reaction kinetics, diffusion or any other rate process.

The First Law of Thermodynamics— The first law of thermodynamics is simply the law of conservation of energy. This law has been stated in various ways but the basic idea is that energy can be neither created nor destroyed ; the only change which energy can undergo is a transformation from one form to another. Hence it follows that *the energy of an isolated system remains constant and whenever a quantity of some form of energy disappears, an exactly equivalent quantity of some other forms of energy must be produced.*

The law of conservation of energy whose truth appears almost axiomatic to us now, was rather slow to be accepted. In fact it encountered more opposition than the second law, and numerous were the attempts to construct *a perpetual motion machine* which would produce work for eternity without any fuel. The law was first clearly stated by Mayer in 1842 and after Joule's classical researches (1845) on the equivalence between heat and work, it was generalised by Helmholtz in 1847.

Mathematical Formulation of the First Law— Suppose we put some amount of heat in a system. Since the heat energy cannot be lost, it must remain either wholly or partly as internal energy in the system, or can be wholly or partly used up by the system in doing mechanical work. In the general case when the

heat absorbed goes both to increase the internal energy and to produce some mechanical external work, we must have

Heat absorbed=Increase of internal energy+Work done by the system.

or, *Increase of internal energy* $\Big\}$ = *Heat absorbed* − $\Big\{$ *Work done by the system.*

If the final and the initial internal energies of the above system are E_2 and E_1 respectively, then the increase in internal energy is $E_2-E_1=\triangle E$ (the symbol $\triangle$ always signifies increase *i.e.* final—initial); if the heat *absorbed* is q and the work done *by* the system is w, then by substituting these values in the foregoing equation we get

$$\triangle E=q-w \qquad \dots \qquad \dots \qquad \dots \text{(1)-VIII}$$

which is the first law of thermodynamics.

If the above change as shown in equation (1) is very small we can write the above quantities in infinitesimals, *i.e.*

$$dE=dq-dw \qquad \dots \qquad \dots \text{(2)-VIII}$$

If the system is under a pressure P and increases by a small volume dV, the work done is pressure multiplied by volume change *i.e.* $P.dV$, and therefore the foregoing equation becomes

$$dE=dq-P.dV \qquad \dots \qquad \dots \text{(3)-VIII}$$

This is the mathematical expression for the first law for infinitesimal changes where the work is exclusively of the pressure ∺ volume type.

Example 1—*Two identical watch springs one of which is completely coiled and the other is uncoiled are dissolved in acid. Will there be a difference in the heat liberated in the two cases?*

The coiled spring contains more energy and since the final conditions are the same, more heat will be liberated in the former case. This also follows from equation (1) because the only difference between the two cases is that E_1 in the former case is higher and therefore q is lower and therefore −q, the heat evolved, is higher.

N.B.—It is to be carefully noted that we have used the convention of expressing q as heat *absorbed* and w as work done *by* the system and so, in our convention −q is the heat *evolved* and −w is the work done *upon* the system.

Example 2—*One gram water at 100°C requires 536 calories of heat for conversion into steam at 100°C. Calculate the increase in internal energy per mol. of water assuming water vapour to behave as an ideal gas.*

$q=536\times 18$ cal/mol$=9648$

$w=PV=RT=2\times373=746$ calories

∴ $\triangle E=q-w=9648-746=8902$ cal/mol.

Mathematical Implication of the First Law Equation—The mathematical significance of this simple equation (1) is much deeper than is apparent. This equation means that if a system changes from a certain initial state to a certain final state,—which it can do in an infinite number of ways,—the increase in

internal energy is always the same by whatever way the change is brought about, although the heat absorbed or the work done by the system might vary with the path by which the change is effected. The quantity E, the internal energy, is thus a characteristic of the state of the system and is not dependent on the way in which that state has been reached. This is shown graphically in Fig. 37, where $\triangle$E is the same and is equal to $E_B - E_A$, whether the change takes place by path (1) or by path (2) or by any other path.

The above fact is expressed in mathematical parlance by saying that E is a *state function*, i.e. its value depends solely on the state of the system and not the least on its previous history. So, E can be differentiated and dE can be integrated by standard mathematical techniques.
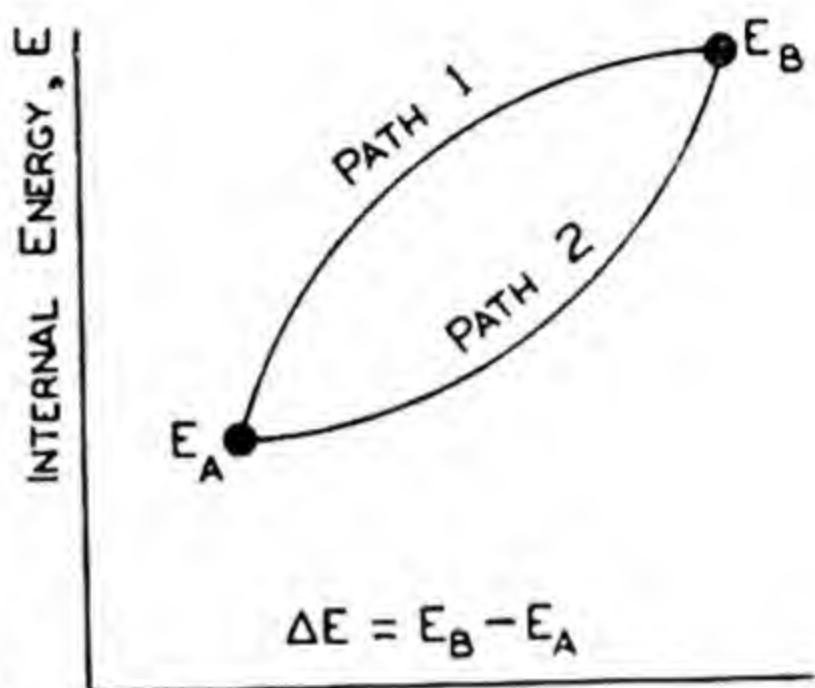

$$\Delta E = E_B - E_A$$

Fig. 37—Internal energy as a function of state.

It may be pointed out that not all properties are state functions and so they do not admit of general differentiation and integration. For example, q and w in equation (1) are not functions of the state but depends on how that state has been arrived at. So q cannot be differentiated and dq cannot be integrated except under special conditions. This is often expressed by saying that dq is not a perfect differential and some fastidious writers even object to writing dq and dw in equation (2). However, we shall continue to use them keeping in mind that they are not perfect differentials.

(a) **Cyclic process**—From what has been said it follows that if a system passes from A to B by two or more different paths, $\triangle$E$=E_B - E_A$, is the same for all the paths. Hence, if it goes *via* path (1) and comes back *via* path (2), it completes a cycle and the overall change of E *i.e.* $\triangle$E for the whole cycle is zero. Applying this on equation (1), we immediately see that

q (for the whole cycle)$=w$ (for the whole cycle)   (4)-VIII.

Hence, we arrive at the very important relation that *in any complete cycle of operations the algebraic sum of all the heat terms is equal to the algebraic sum of all the work terms.* [For an illustrative example *vide* Exercise (10)].

(b) **Changes at constant volume**—If there is no volume change, $dV = O$ and the above equation (3) reduces to $dE = dq$ i.e. *the heat absorbed by the system at constant volume goes completely to increase the internal energy of the system*, provided of course, no other type of work but of the pressure $\times$ volume type is involved.

(c) **Adiabatic changes**—An adiabatic change is one in which the system is allowed neither to gain heat from, nor to give out heat to the surroundings at any stage of the change. Such a change could not be realised in practice since there is no perfect insulator of heat to make a heat-tight vessel for such experiments. However, many actual processes are close approach to this type of behaviour; for example, when sound passes through air, the compressions and rarefactions occur so rapidly that for all practical purposes these may be regarded as adiabatic processes. Despite all this, much use is made of adiabatic processes in thermodynamic reasonings.

Since heat is not allowed to enter or leave the system in an adiabatic process, we have $q=0$ and therefore,

$$-\triangle E = w \text{ (for an adiabatic process)} \qquad \text{... (5)-VIII}$$

i.e. under adiabatic conditions, the decrease in internal energy is equal to the work done by the system.

The Heat Content or Enthalpy of a System—It is often convenient, particularly to deal with systems at constant pressure to use a function H, called the heat content or enthalpy in place of the internal energy E, the two being related by the equation,

$$H = E + PV \qquad \text{...} \qquad \text{...} \qquad \text{... (6)-VIII}$$

Since E is a characteristic of the system according to the first law, it immediately follows from the above definition of H, that H is also a similar function whose value depends only on the initial and the final conditions of the system. If the final heat content is H_2 and the initial value is H_1 then we have,

$$\triangle H = H_2 - H_1$$
$$= (E_2 + P_2V_2) - (E_1 + P_1V_1)$$
$$= (E_2 - E_1) + (P_2V_2 - P_1V_1) \qquad \text{... (7)-VIII}$$
$$= \triangle E + \triangle(PV)$$

If the pressure is constant, this reduces to

$$\triangle H = \triangle E + P(V_2 - V_1) = \triangle E + w = q_p \qquad \text{... (8)-VIII}$$

Therefore, $\triangle H$ *i.e.* increase in H is equal to the heat *absorbed* at constant pressure, q_p and this explains the name, heat content for the function, H. However, if the pressure on the system is not constant, $\triangle H$ is not equal to the heat absorbed and is to be calculated from equation (7).

Joule's Experiment. Internal Energy of an Ideal Gas—Joule in 1844 allowed a gas to expand freely into a vacuum and observed that the system as a whole neither gained nor lost heat. He took two metallic flasks connected by a stopcock one of which contained a gas under pressure and the other was evacuated. (Fig. 38). He put the whole thing under water and opened the stopcock. After the gas had expanded to fill completely both

the flasks at equal pressure he measured the temperature of the,
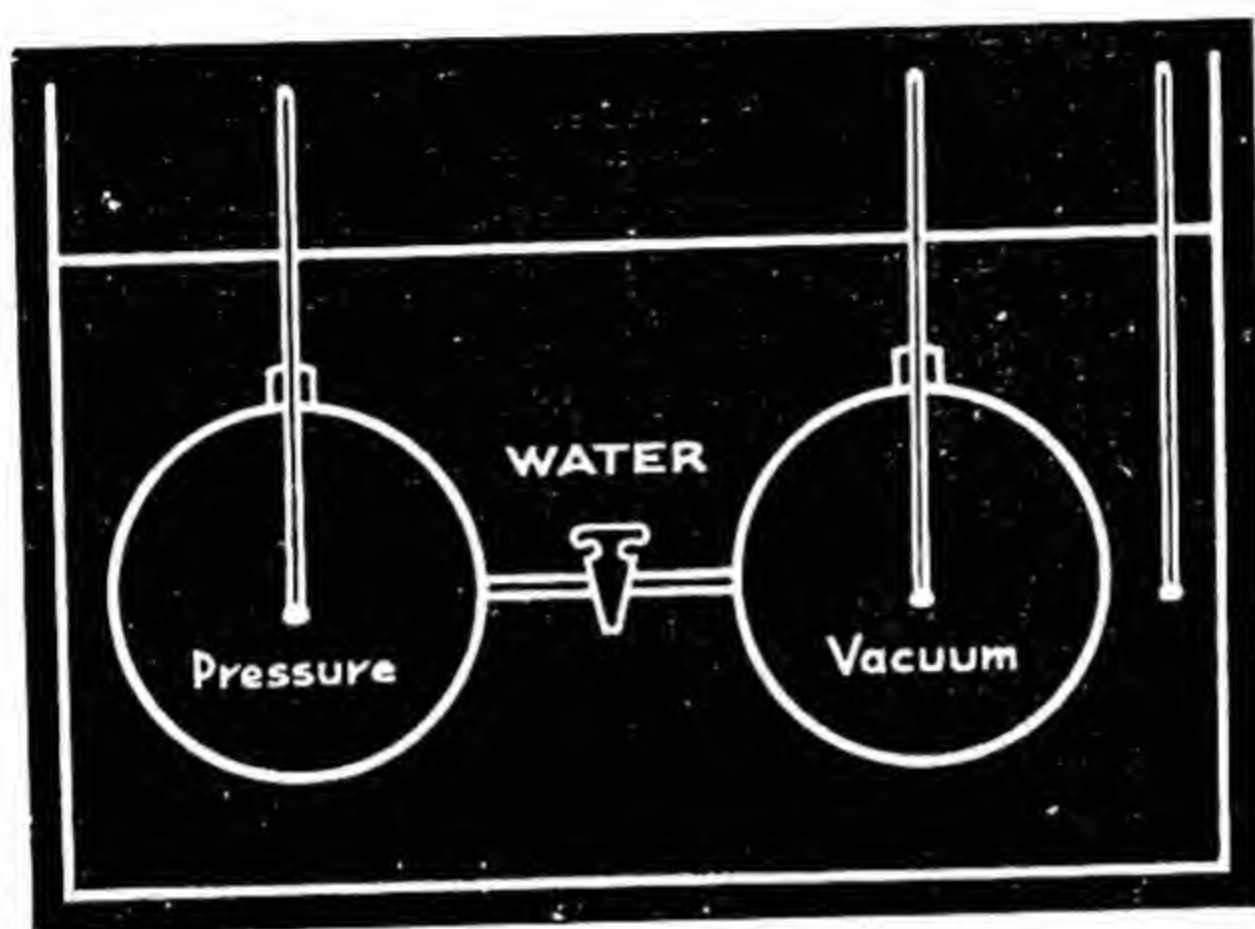water. He failed to observe any noticeable temperature change of

Fig. 38—Joule's Experiment.

the water from which he concluded that the internal energy of a
gas is independent of the volume at constant temperature.

This conclusion is easily arrived at by applying the first law,
to the above experiment. In the equation, $\triangle E = q - w$, we
observe in the present case that q is zero since no heat is evolved
or absorbed from the surroundings as noted by the thermometer,
and w also is zero since no mechanical work has been done as the
gas has expanded against zero pressure. Hence, $\triangle E = 0$. If the
gas was allowed to expand only by a small volume, dV in the
above experiment, we could immediately write the result as

$$\left[\frac{\partial E}{\partial V}\right]_T = 0 \qquad \ldots \qquad \ldots \quad (9)\text{-VIII}$$

i.e. the internal energy of a perfect gas is independent of the
volume. For actual gases there is, however, a slight increase or
decrease of temperature, but for a perfect gas which has no inter-
molecular attraction, the above is strictly valid.

Joule-Thomson Experiment—In the foregoing experiment
of Joule, E, the internal energy was constant. Such is, however,
not the case if the gas expands against a constant pressure as
was done in the porous plug experiment of Joule-Thomson. A
gas at a pressure P_1 was forced through a porous plug in a thermally
insulated tube against a pressure P_2 which is obviously lower
than P_1. This process was conducted slowly so that the pressures
were maintained steady on both sides at P_1 and P_2 respectively
and the temperature difference between the two sides was

7

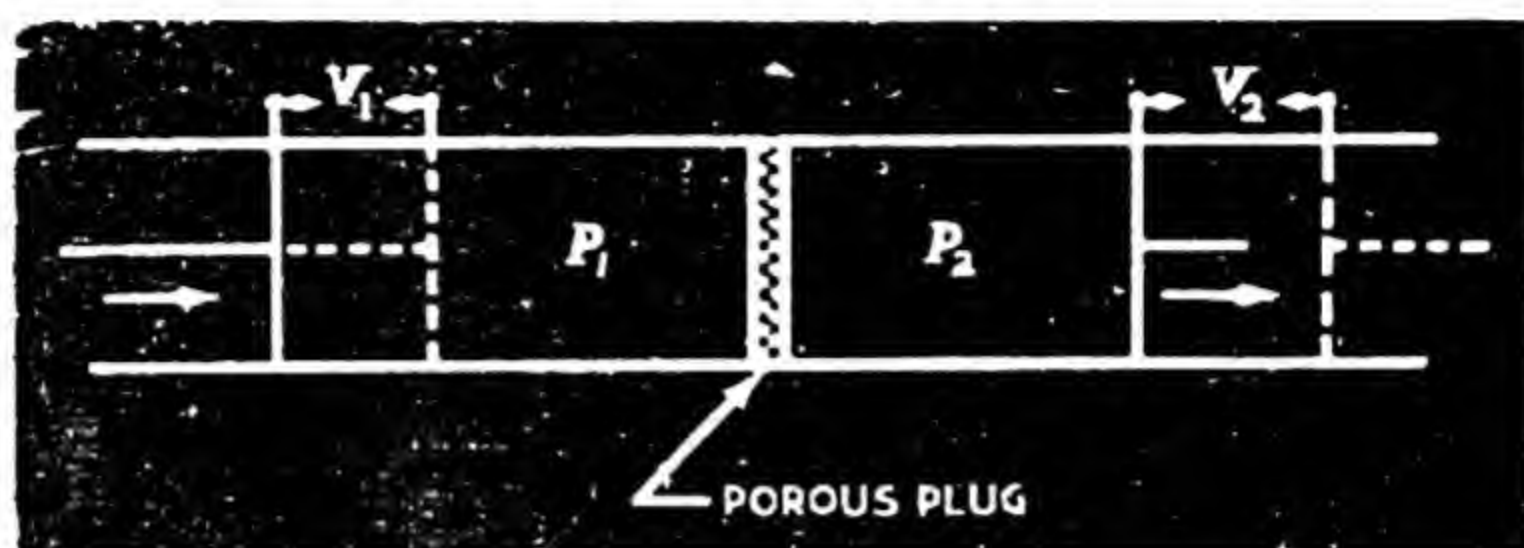measured. It was observed that most gases cooled down by such

Fig. 29—Joule-Thomson Porous Plug Experiment

a pressure drop, whereas hydrogen at ordinary temperature warmed up.

Explanation of Joule-Thomson Effect—The Joule-Thomson cooling may be regarded as due the fact that real gases are not perfect from two aspects, viz. their failure to strictly conform to Boyle's law and Joule's law. Firstly, Boyle's law being not strictly valid P_2V_2 is not equal to P_1V_1, which means that the work done on the gas in pushing it through the plug, is not equal to the work done by the gas while issuing out on the other side. This extra work is obtainable only at the expense of the internal energy of the gas and so the gas cools. Secondly, the gas may not satisfy Joule's criterion of a perfect gas (eqn. 9). There may be intermolecular attraction and work has to be spent during increase of volume to overcome this attraction. This extra work necessarily has to be provided out of the internal energy of the gas, as a result of which the gas cools on Joule-Thomson expansion.

Proof of Constancy of H in Joule-Thomson Expansion—Since the system is thermally insulated, the system can neither absorb nor give out heat to the surroundings; hence $q = 0$. Also, the gas in expanding does work equal to $P_2V_2 - P_1V_1$. Substituting these values of order in the first law equation, $\Delta E = q - w$, we get,

$$\Delta E = 0 - (P_2V_2 - P_1V_1)$$
$$E_2 - E_1 = -P_2V_2 - P_1V_1$$
$$\text{or } E_2 - P_2V_2 = E_1 - P_1V_1$$
$$\therefore H_2 = H_1 \qquad\qquad 10\text{-(VIII)}$$

Since the heat content H is defined by the equation $H = E + PV$, the above equation reduces to $H_2 = H_1$. We hence conclude that *in adiabatic expansion of any real gas its heat content remains constant.*

Data on Joule-Thomson Cooling—Hence, if the gas in the above free expansion falls in temperature dT by a lowering of pressure dP, we may define the Joule-Thomson coefficient μ, by the expression

$$\mu = \left[\frac{dT}{dP} \right]_H$$

The significance of μ might be taken as the drop in temperature in degrees experienced by a gas in free expansion by a pressure drop of one atmosphere under adiabatic conditions. The experimental values of μ for a few gases are shown in the following table. The value of μ can be easily shown to be zero for a perfect gas, *i.e.* a gas whose equation of state is PV=RT. For a gas obeying van der Waals equation, the Joule-Thomson coefficient, μ is given by the expression,

$$\mu = \frac{2a}{RT} - b \text{ (for a van der Waals gas)}$$

in agreement with the fact that the higher the intermolecular attraction 'a', the more is the Joule-Thomson cooling. As pointed out in Chapter V, Joule-Thomson effect is of great technical importance in the liquefaction of gases.

Gas	Temp.	μ	Gas	Temp.	μ
Hydrogen	0°C	−0·03	Carbon dioxide	0°C	1·35
Oxygen	,,	0·31	,,	40°C	0·96
Air	,,	0·27	,,	100°C	0·62

It should be noted that hydrogen has a negative μ showing that it warms up on expansion. This circumstance was responsible for causing many accidents owing to self-ignition of highly compressed hydrogen leaking through damaged pipelines. It should also be noted from the data on carbon dioxide that generally the lower the temperature, the more is the cooling effect on expansion.

Heat Capacity—When any substance is heated, the amount of heat necessary to raise its temperature by 1°C is different if it is heated at constant volume from what is needed if the heating is done at constant pressure. Suppose we heat a mol of a substance at constant volume through a temperature dT. The amount of heat (dq) necessary is $C_v dT$ where C_v is the heat capacity at constant volume. Since the substance does no external work the whole amount of heat goes to increase the internal energy. Hence, we should have

$$dE = C_v dT \quad or, \quad C_v = \left(\frac{\partial E}{\partial T}\right)_V \quad \dots \quad \dots \text{ (11)-VIII}$$

If, however, the substance is heated at constant pressure, P, the work done is PdV, and the heat absorbed (dq) is $C_p dT$ where C_p is the heat capacity at constant pressure. These values substituted in the first law equation (3) gives

$$dE = C_p dT - P.dV$$
$$C_p dT = dE + P.dV$$

$$C_p = \left(\frac{\partial (E+PV)}{\partial T}\right)_P$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \quad \cdots \qquad \cdots \qquad \cdots \text{(12)-VIII}$$

These two equations (11) and (12) are the thermodynamic definitions of C_v and C_p.

The Difference, $(C_p - C_v)$—From the above expressions for C_p and C_v their difference can be easily obtained in terms of other measurable quantities. The method employs a well-known procedure in partial differentiation which is very often used in thermodynamics. From equations (11) and (12) we have

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V \cdots \qquad \cdots \text{(13)-VIII}$$

But from definition (eqn. 6), $H = E + PV$, which on differentiation with respect to temperature at constant pressure gives

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

This substitution in the previous equation gives

$$C_p - C_v = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V \quad \cdots \text{(14)-VIII}$$

Now the question is to find a relationship between the first and the last term. Since, the energy E is a function of only two variables, say, volume, V and temperature T, any increment of E can be expressed as due to the latter two factors separately as in the following equation.

$$dE = \left[\frac{\partial E}{\partial T}\right]_V dT + \left[\frac{\partial E}{\partial V}\right]_T dV$$

The significance of this equation is that if a substance undergoes a small increase of temperature dT and a small increase of volume dV, the total increase of internal energy dE may be divided into two parts, the first one as due to the increase in temperature alone the volume being kept constant, and the other one as due to the increase of volume alone, the temperature being kept constant. The student should not have any difficulty in treating the partial derivatives if he remembers that they are like algebraic constants, a, b, etc. and have definite values under definite conditions.

Dividing by dT throughout and imposing the restriction of constancy of pressure, we get

$$\left[\frac{\partial E}{\partial T}\right]_P = \left[\frac{\partial E}{\partial T}\right]_V + \left[\frac{\partial E}{\partial V}\right]_T \left[\frac{\partial V}{\partial T}\right]_P$$

Substituting this value in equation (14) we have

$$C_p - C_v = \left[\frac{\partial E}{\partial V}\right]_T \left[\frac{\partial V}{\partial T}\right]_P + P\left[\frac{\partial V}{\partial T}\right]_P \qquad \dots \text{ (15)-VIII}$$

$$= P\left(\frac{\partial V}{\partial T}\right)_P \left[1 + \frac{1}{P}\left(\frac{\partial E}{\partial V}\right)_T\right] \qquad \dots \text{ (16)-VIII}$$

This equation is a perfectly general one and holds for any substance whatsoever. With the help of second law this equation can be transformed into the following equation which is very convenient for application to experimental data.

$$C_p - C_v = \alpha^2 VT/\beta \qquad \dots \qquad \dots \text{ (17)-VIII}$$

where α is the co-efficient of cubical expansion and β is the compressibility.

APPLICATION OF FIRST LAW TO IDEAL GASES

What Constitutes an 'Ideal' Gas —We have already laid down the conditions of ideality of a gas. They are:—

(1) An ideal gas should follow the equation $PV = RT$ under all circumstances (Ch. II); and

(2) The internal energy of an ideal gas is a function of temperature alone (Joule's experiment), *i.e.*

$$\left[\frac{\partial E}{\partial V}\right]_T = O \quad \text{and} \quad \left[\frac{\partial E}{\partial P}\right]_T = O$$

These two are necessary and sufficient conditions of ideality of any fluid.

$C_p - C_v$ for an Ideal Gas —Applying Joule's criterion of a perfect gas, *viz.* $(\partial E/\partial V)_T = 0$, on equation (16) we obtain

$$C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_P \qquad \dots \qquad \dots \text{ (18)-VIII}$$

But, for an ideal gas $PV = RT$, which on differentiation at constant pressure gives

$$P\left[\frac{\partial V}{\partial T}\right]_P = R \quad \therefore \quad C_p - C_v = R \qquad \dots \qquad \dots \text{ (19)-VIII}$$

This equation has been already deduced from the kinetic theory of gases (Ch. II).

Isothermal and Adiabatic Expansion—When a perfect gas expands adiabatically i.e. $q = 0$, the first law equation $\triangle E = q - w$, becomes $-\triangle E = w$ i.e. the work done by the gas is equal to the decrease in internal energy of the gas. Since internal energy of an ideal gas depends only on the temperature, the decrease in

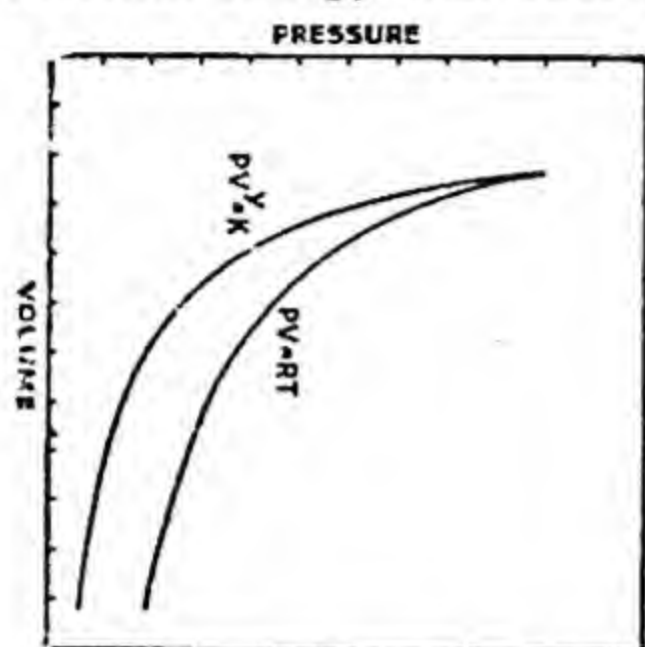internal energy will cause the gas to fall in temperature. There-
fore, we conclude that the gas will be cooled by an adiabatic expansion. We also 'see that this cooling effect will cause the final volume to be lower than what it would have occupied if the expansion was conducted isothermally. In other words, if the pressure and volume are plotted on a P–V diagram, *the adiabatic curve should be steeper than the isothermal one* as shown in the diagram. The actual relationship among P, V and T in an adiabatic expansion can be obtained thermo-dynamically.

Fig. 40—Isothermal and Adiabatic expansion of a perfect gas.

Suppose we have one mol of an ideal gas which expands adiabatically (*i.e.* $q=0$) by a very small increase of volume, dV. Since the volume increase is infinitesimally small the work done by the gas is PdV, and hence from eqn. (5) $dE = -P.dV$ ... (2)

Also, since the internal energy of an ideal gas does not depend on the volume, the equation (11), $C_v = (\partial E/\partial T)_V$ reduces to

$$dE = C_v dT$$

Substituting this value of dE in equation (20), and $P=RT/V$ which is always applicable to an ideal gas we have

$$C_v dT = -P.dV = -\frac{RT}{V} dV \qquad \cdots \qquad \cdots \quad (21)\text{-VIII}$$

$$\text{or} \quad \frac{C_v}{R} \frac{dT}{T} = -\frac{dV}{V}$$

Considering C_v a constant independent of temperature and integrating within limits we have

$$\frac{C_v}{R} \int_1^2 \frac{dT}{T} = -\int_1^2 \frac{dV}{V}$$

$$\text{or} \quad \frac{C_v}{R} \ln (T_2/T_1) = -\ln (V_2/V_1)$$

Now, $R/C_v = (C_p - C_v)/C_v = \gamma - 1$

$$\therefore \ln (T_2/T_1) = -\ln (V_2/V_1)^{\gamma-1}$$

$$\therefore \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1} \qquad \cdots \qquad \cdots \quad (22)\text{-VIII}$$

If we want the correlation between P and V we can do this by eliminating dT between equation (21) and $PV=RT$ as shown

below. The latter equation on differentiation gives

$$PdV + VdP = RdT$$

also

$$-PdV = C_v dT$$

Eliminating dT we have, $PdV + VdP = R(-P.dV/C_v)$

$$PdV(1 + R/C_v) = -VdP$$

which on simplification with the help of the already established relation, $C_p - C_v = R$ and subsequent integration gives,

$$\gamma \frac{dV}{V} = -\frac{dP}{P}$$

$$PV^\gamma = \text{constant} \qquad \ldots \qquad \ldots \quad (23)\text{-VIII}$$

where γ is the ratio C_p/C_v. This is the desired relation.

By an essentially similar process we can eliminate V and obtain the pressure-temperature relationship in an adiabatic process. The three equations under adiabatic conditions for a perfect gas are—

(i) $\left(\dfrac{V_1}{V_2}\right)^{\gamma-1} = \dfrac{T_2}{T_1}$ (ii) $P_1 V_1{}^\gamma = P_2 V_2{}^\gamma$; (iii) $\left(\dfrac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \dfrac{T_2}{T_1}$

$$\ldots \qquad \ldots (24)\text{-VIII}$$

These equations can be more conveniently expressed in their logarithmic forms. For example equation (iii) after taking logarithm of both sides becomes

$$\frac{\gamma-1}{\gamma} \log (P_2/P_1) = \log (T_2/T_1)$$

which is very suitable for purpose of calculation.

Example 3—*Calculate the increase of temperature if helium at 0°C is compressed adiabatically to half its volume.*

Now, $\gamma = 1.66$, $V_1/V_2 = 2$, which substituted in equation (22) gives

$(2)^{0.66} = T_2/273$ or $T_2 = 273 \times (2)^{\frac{3}{3}} = 433.7°K = 160.7°C$.

Note the large rise of temperature.

EXERCISES

1. When ice melts at 0°C, the latent heat of fusion is 80 calories per gram. The density of ice is 0·82 and of water is unity. Calculate $\triangle E$, $\triangle H$, q and w per mol.
[1440·1 cals, 1440 cals, 1440 cals, $-4·01 \times 10^6$ ergs.]

2. Calculate the same quantities in the conversion of water into steam at 100°C, given that one gram of steam occupies 1676 c.c. and the volume of water can be neglected in its comparison (latent heat :—537 cal/gm.)
[8934·2 cals, 9666, 9666 cals, 30587×10^6 ergs.]

3. Calculate the rise in temperature of a piece of copper ($C_p = 6·4$) when dropped from the top of Qutab Minar (height 270 ft.) assuming no heat is lost.
[1·91°C]

4. When coal gas burns in a Bunsen burner, is the heat effect observed equal to $-\triangle H$ or $-\triangle E$?

5. When a toy balloon is warmed it increases in size. Formulate the first law equation for the process and indicate how the $\triangle H$ for the process is connected with the heat supplied to the system.

6. Calculate $\triangle E$ and $\triangle H$ if 10 litres of helium at N.T.P. are heated inside a gas cylinder to 100°C assuming it to behave ideally and having $C_v = \frac{\cdot}{2} R$. [133·8; 223·1]

7. If a liquid or a gas is compressed from one to 20 atmospheres, which one will be closer to an adiabatic process, a slow compression or a rapid one? Compression of a large quantity or a small quantity. Discuss fully.

8. A mol of an ideal gas at 0°C is compressed reversibly and adiabatically from 1 atm. to 2 atm. What is the final temperature if $C_v = 3$ cal/°C. [87·1]

9. Ten mols of nitrogen at 0°C under 20 atm. is suddenly released of its pressure to 3 atm. and the gas expands adiabatically. If C_p for nitrogen is 7 calories per deg., and the gas behaves ideally, calculate the final temperature. Calculate also $\triangle E$ and $\triangle H$ for the process. [158·9°K. −5705; −7987 cal.]

10. A mol of monatomic ideal gas is heated at constant volume from 25°C and 1 atm. to 500°C. The gas is now isothermally and reversibly expanded to its original pressure of one atm. The gas is now cooled at constant pressure to its original temperature of 25°C, thus completing a cycle. Graphically describe this cyclic process on a P−V diagram as also on a T−V diagram. Calculate q and w for each step and for the whole cycle. [$q_1 + 1425$ cals. $q_2 = 1474$ cal. $q_3 = -3325$ cals. $w_1 = 0$. $w_2 = 6162 \times 10^7$ ergs; $w_3 = 394 \times 10^8$ erg.]

CHAPTER IX

THERMOCHEMISTRY

General—It is a common experience that chemical reactions, in general, are attended with either evolution or absorption of heat. In some reactions, *e.g.* the burning of magnesium ribbon or the combination of chlorine with hydrogen, iron, etc. the associated thermal change is too large to be overlooked.

The basic theoretical guide to a study of the heat changes of chemical reactions is, of course, the first law of thermodynamics but, the subject was under vigorous study long before the first law was established as an irrevocable truth, and so, many principles had to be discovered by the earlier workers which we know to be inherent in the first law itself.

Heat of Reaction : Exothermic and Endothermic Changes— —*Reactions which take place with liberation of heat are called exothermic reactions, whereas reactions which take place with absorption of heat are endothermic.* If any reaction is endothermic it follows that the reverse reaction is exothermic and it is usually found—though not always—that exothermic reactions proceed spontaneously and vigorously.

The amount of heat which is evolved when a reaction takes place at constant volume indicated by and between the amounts of substances shown in the equation is called its heat of reaction. Thus, the expression—the heat of reaction in the formation of hydrochloric acid according to the equation, $H_2 + Cl_2 = 2HCl$ is 43,600 calories—means that when 2 gms of hydrogen combine with 71 gms of chlorine to form 73 gms of HCl, the amount of heat liberated is 43,600 calories.

Measurement of Heat of Reaction—Heats of reactions are directly measurable only for reactions which are quite fast and run to completion along a well-defined course, and these are usually determined by calorimetric experiments. The reacting substances are allowed to combine in a calorimeter, if they are liquids or solids, or in a closed bomb if any of them is gaseous and the whole is kept immersed in a large vessel full of water. Noting the temperature increase of the water after the reaction is complete and knowing the heat capacities of the different parts of the apparatus, the heat of reaction is easily calculated.
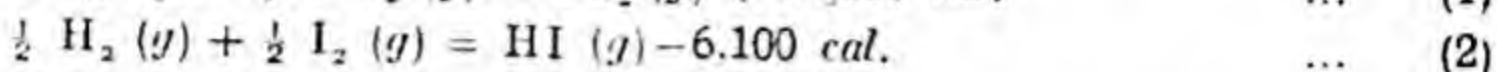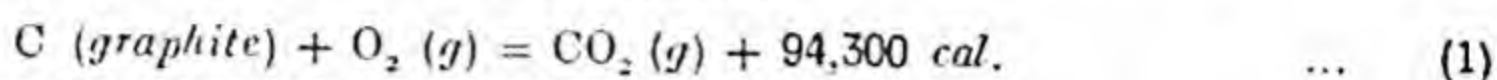
Notations and Conventions—It is customary to follow the convention of adding with a *positive sign* in the side of the products, the amount of heat which is *evolved* in a chemical reaction. Thus, in the general equation,

$$A + B = C + D + Q \text{ Cals.}$$
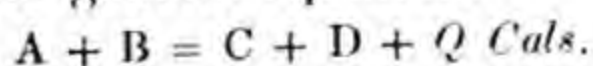
Q is called the heat of reaction. It should be carefully noted that Q has a positive value where heat is evolved and a negative

value when heat is absorbed. This is just the opposite of the convention followed in the previous chapter.

Since the heat of reaction evidently depends on the state of aggregation, this is indicated in the energy equation by using g for the gaseous state, l for liquids and s for solids, whenever there is any chance of confusion. Also, for elements exhibiting allotropy, the allotropic form is to be indicated.

$$C \ (graphite) + O_2 \ (g) = CO_2 \ (g) + 94,300 \ cal. \qquad \ldots \quad (1)$$
$$\tfrac{1}{2} H_2 \ (g) + \tfrac{1}{2} I_2 \ (g) = HI \ (g) - 6.100 \ cal. \qquad \ldots \quad (2)$$

Thus, equation (1) signifies that if a gram atom of carbon in the form of graphite is oxidised completely with gaseous oxygen to form gaseous carbon dioxide at constant volume, 94,300 calories are *evolved*. Similarly equation (2) shows that 6,100 calories are *absorbed* to form a mol of HI gas from H_2 and I_2 in the gaseous state. For very precise work it is also necessary to specify the temperature but it is generally not done in energy equations and the data are usually at $25°C$. If the substance used be in dilute solution, usually the suffix *aq.* is added to the symbol. Some authors use the symbol Cal or Kcal, or Kg.-cal for 1000 gm.-calories of heat.

Modern Nomenclature —In modern scientific literature thermochemistry is regarded as a part of thermodynamics and so the consistent system of thermodynamic notation is used in thermochemical equations. When one mol of hydrogen and half a mol of oxygen react at $25°C$ and 1 atmosphere, 68,400 calories of heat are evolved as shown by

$$H_2 + \tfrac{1}{2} O_2 = H_2O + 68,400 \ cal.$$
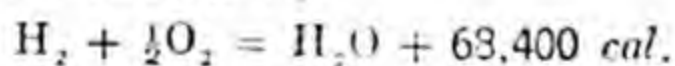
But suppose we look from the point of view of what change the system has undergone. The system in going from the left-hand side to the right-hand side has lost its heat content by 68,400 calories. Since the decrease in heat content at constant pressure, which is generally expressed in thermodynamics as a decrease in the heat content function (H), has been demonstrated (*vide* Ch. VIII, p. 96) to be equal to the negative of the heat of reaction at constant pressure, we can immediately write that the decrease in heat content, $-\triangle H = 68,400$ calories in this case ; or, as usually expressed

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l) ; \quad \triangle H_{298} = -68,400 \ cal.$$
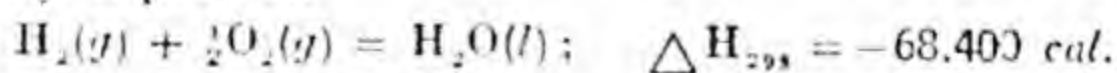
In other words, we first write the equation for the reaction and show the value of $\triangle H$ separately as the negative of the heat of reaction at constant pressure.

The subscript (298 in this case) denotes the temperature in °K. Sometimes a superscript zero is used, for example, $\triangle H°_{298}$, which simply indicates that the reactants and products are under standard conditions, *i.e.* conventionally in their stablest form at $25°C$ and under one atmosphere pressure. Of course, the equations thus written along with the $\triangle H$ values admit of algebraic

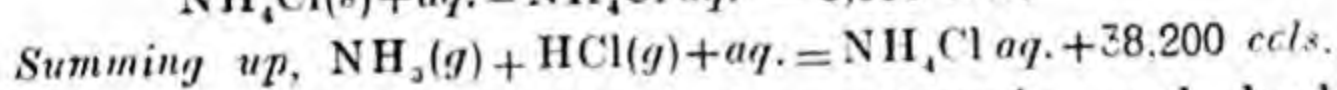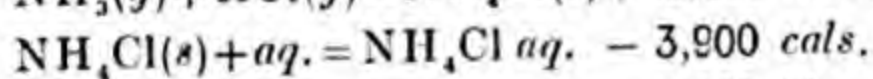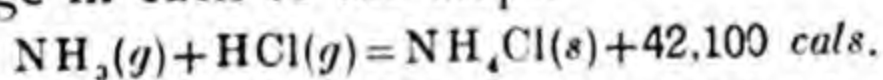procedures like addition, subtraction, elimination, etc. in the same way as our usual thermochemical equations.

Note carefully that $\triangle H$ has a sign opposite to the heat of reaction, Q i.e. exothermic reactions have negative $\triangle H$ and endothermic reactions have positive $\triangle H$ values; also, $\triangle H$ refers to constant pressure conditions whereas Q is usually at constant volume.

Hess's Law of Constant Heat Summation—As a result of experimental researches extending over a number of years Hess showed that the amount of heat evolved or absorbed in a chemical change is independent of the rate of reaction or of the nature of the intermediate compounds, provided the reactants and resultants are the same. This is expressed by Hess's Law, first stated in 1840, as follows:—*If a chemical reaction is brought about in a single step or alternatively, in a number of intermediate steps, the total amount of heat evolved is the same provided the initial and the final stages are the same in all cases.*
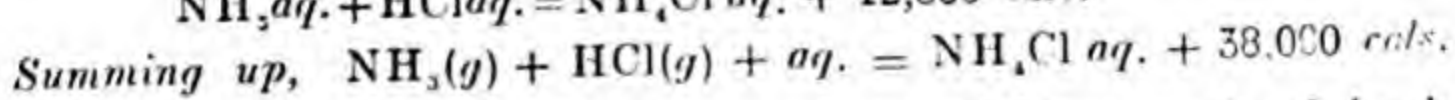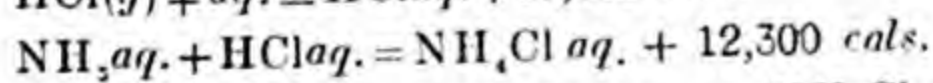
Thus, taking a simple case, if we could burn carbon first into carbon monoxide, and then burn this carbon monoxide to carbon dioxide, the sum of the heats evolved in these two processes would together be equal to the heat of combustion of carbon directly to carbon dioxide.

A simple example to demonstrate the truth of this law is to calculate the heat of reaction when gaseous ammonia and hydrochloric acid are converted into a dilute aqueous solution of ammonium chloride. This can be done in two ways as shown below.

First process—We can mix ammonia gas and HCl gas to form solid ammonium chloride and dissolve it in water to get the aqueous solution of ammonium chloride and note the heat change in each of the steps.

$$NH_3(g) + HCl(g) = NH_4Cl(s) + 42,100 \ cals.$$
$$NH_4Cl(s) + aq. = NH_4Cl \ aq. - 3,900 \ cals.$$

Summing up, $NH_3(g) + HCl(g) + aq. = NH_4Cl \ aq. + 38,200 \ cals.$

Second process—Alternatively, ammonia and hydroch'oric acid gas may be separately dissolved in water and the two solutions mixed to get an aqueous solution of ammonium chloride and the thermal change in each step may be determined.

$$NH_3(g) + aq. = NH_3 aq. + 8,400 \ cals.$$
$$HCl(g) + aq. = HCl aq. + 17,300 \ cals.$$
$$NH_3 aq. + HCl aq. = NH_4Cl \ aq. + 12,300 \ cals.$$

Summing up, $NH_3(g) + HCl(g) + aq. = NH_4Cl \ aq. + 38,000 \ cals.$
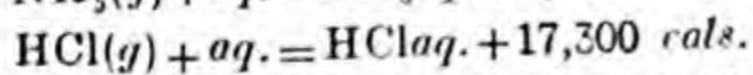
It will be seen that the net amount of heat evolved in both the methods is the same, within the limits of experimental error.

Hess's Law is a direct corollary to the law of conservation of energy, but it had to be discovered experimentally since at that

time the law of conservation of energy had not taken a firm root in the mind of chemists as an absolute truth.

Applications of Hess's Law —The main contributions of Hess's law have been that it allows us to regard thermochemical equations just like algebraic equations admitting of addition, subtraction, elimination, etc., as a result of which we can calculate many heats of reactions which are not experimentally measurable directly owing to slowness or incompleteness of the reactions. The whole chapter is replete with such applications.

A special case of such applications is in the determination of the *heat of transition* of one allotropic modification to another.

2,386 cals

YELLOW P   PHOSPHORIC ACID

2,113 cals

............RED P

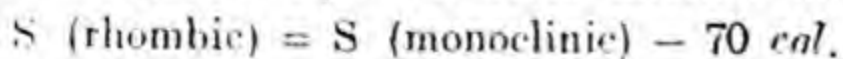∴   YELLOW P————————→RED P + 273 calories.
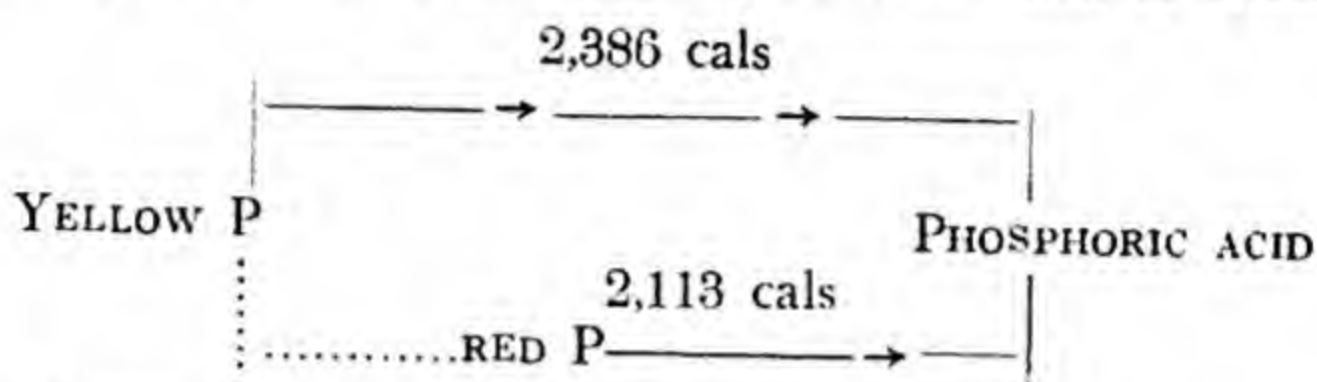
The case of conversion of yellow phosphorus to red phosphorus may be cited as an example. Though the heat of conversion is not directly measurable here, it can still be calculated on the basis of Hess's law, in the following way:—one gram atom of yellow phosphorus on oxidation to phosphoric acid yields 2386 cals of heat. Red phosphorus on similar treatment yields 2113 cals of heat. Therefore, according to Hess's law this difference in the heats of reaction represents the heat of conversion of yellow to red phosphorus which is therefore equal to 273(= 2386 − 2113) cals. Similarly, the heat of transition of rhombic to monoclinic sulphur, or graphite to diamond can be computed as shown by a simple exercise below.

Example 1. *The heats of combustion of rhombic S and monoclinic S are 70,960 and 71,030 calories respectively. Calculate the heat of transition.*

S (rhombic) + O_2 = SO_2 + 70,960 cal.

S (monoclinic) + O_2 = SO_2 + 71,030 cal.
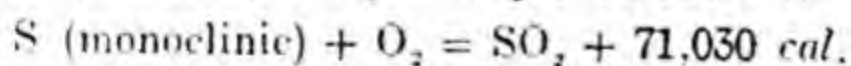
Subtracting one equation from another and transposing, we get,

S (rhombic) = S (monoclinic) − 70 cal.

So, the heat of transition is −70 calories.

Heat of Formation —The heat of formation may be defined as the amount of heat *given out* when a *gram molecule* of the substance is produced from its component elements in the standard state. Thus in the equation, C + O_2 = CO_2 + 94,300 cals., it will be seen that to produce one mol of carbon dioxide from its elements, 94,300 cal. are evolved and so the heat of formation of carbon dioxide is 94,300 cal. Similarly, during the formation of one mol of hydriodic acid gas, 5,920 calories are absorbed;

we may regard this as—5,926 calories being given out, and so, the heat of formation of the gas is—5,926 calories.

Substances formed with absorption of heat are called **endothermic compounds** *while those formed with evolution of heat are called* **exothermic compounds.** So, exothermic compounds have positive heat of formation and endothermic compounds have negative value for it. Almost all common compounds are exothermic, *i.e.* have positive heats of formation with the exception of nitric oxide, hydriodic acid, carbon disulphide, ozone, acetylene and some unsaturated hydrocarbons, etc. The following table gives the heats of formation of a number of compounds.

HEATS OF FORMATION (18°C, 1 *atm., in K-cal/mol.*).

C (Diamond)	−0·22	H_2S (g)	5·3
C (-graphite)	0·00	NO (g)	−21·6
CH_4	18·02	CS_2 (l)	−22·0
C_2H_6	20·74	NH_3 (g)	11·00
C_2H_4	−11·22	H_2SO_4 (l)	193·75
C_2H_2	−54·10	HNO_3 (g)	35·34
C_2H_5OH	66·92	CO (g)	26·62
H_2O (l)	68·37	CO_2 (g)	94·23
HF (g)	64·2	AgCl (s)	30·30
HCl (g)	22·06	NaCl (s)	98·33
HBr (g)	8·65	$ZnSO_4$ (s)	233·4
HI (g)	−5·91	NH_4NO_3 (s)	88·0

Usefulness of Heat of Formation Data—The heat of formation of compounds as such is not of great significance, but their main utility is in the fact that any heat of reaction can be easily calculated with the help of such data for the reactants and products. Thus, instead of tabulating the heats of reactions of all possible chemical reactions, which at any event would require an unmanageably large space, the same purpose would be served from a much smaller compilation of heat of formation data. So, a self-consistant table of heat of formation is a condensed summary of all possible heats of reactions involving the compounds appearing in the table as also all elements. It should be noted that not only actual reactions but also hypothetical or hitherto unknown reactions can be dealt with with the help of such table.

The method of calculation of heat of reaction from heat of formation data will be discussed and illustrated in details in a later section under intrinsic energy.

Heat of Formation of Salts—The heat of formation of a salt may itself be regarded as the resultant heat effect of a number of simpler reactions. For example, we may regard the formation of sodium chloride, starting from sodium and chlorine to be formed by the following steps (*e* means an electron):—

(1) Steps (*a*) and (*a'*)—Conversion of sodium into vapour of atomic sodium and conversion of gaseous chlorine into the atomic state.

(2) Steps (*b*) and (*b'*)—Breaking of the sodium atoms obtained in step (a) into Na+ ion and an electron, and making a Cl⁻ ion from the chlorine atom of step (*a'*) by adding an electron.

(3) Steps (*c*) and (*d*)—Reacting the Na+ ions and Cl⁻ ions obtained in the previous step into NaCl vapour (step *c*) and condensing the NaCl vapour into solid NaCl (step *d*).

(*a*) Na (*solid*)⟶Na (*gas*)−25 Kcal (*a'*) ½ Cl₂ (*gas*)⟶Cl (*gas*)−29 Kcal.

(*b*) Na (*gas*)⟶Na+ + e−119 Kcal (*b'*) Cl (*gas*) + e⟶Cl⁻−92 Kcal.

(*c*) Na+ + Cl⁻ = NaCl (*gas*) + 128 Kcal.

(*d*) NaCl (*gas*) = NaCl (*solid*) + 52 Kcal.

Summing up. Na (*solid*) + ½ Cl₂ (*gas*) = NaCl (*solid*) + 98 Kcal.
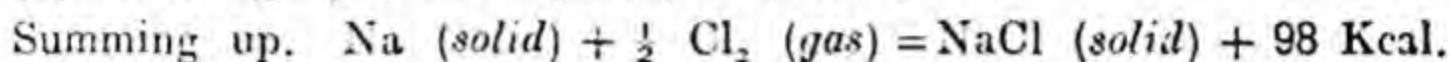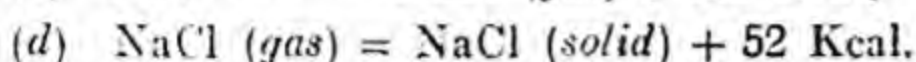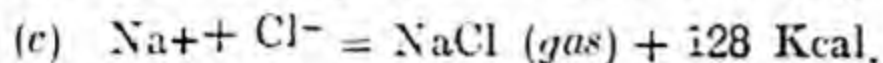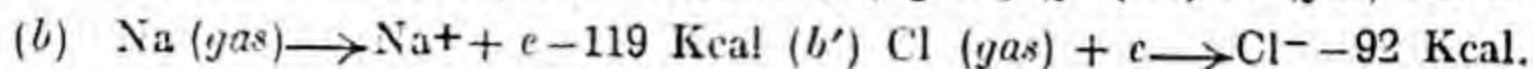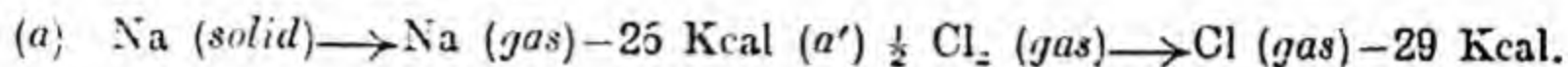
If we analyse the heat of formation of AgCl (30·3 kilocalories) in the same manner it would be observed that the heat effects in most of the steps would be of the same order except the ionisation step (step *b*) where a much larger quantity of heat would be absorbed in conformity with the fact that the electron affinity of silver is higher than that of sodium as is seen by the fact that silver is displaced by sodium in the electrochemical series (*i.e.*, silver is nobler). For example, the electron affinity of sodium as quoted above is 118 Kcal whereas that of silver is 173·7 Kcal. So, we may expect that, as a rough approximation, the heat of formation of salts of the same anion would decrease as the metallic ion becomes nobler. This is actually found to be the case and is illustrated in the following table.

HEAT OF FORMATION OF SALTS

(in Kcal per gm atom of the negative element)

	Chlorides	Iodides	Oxides	Chloride aq.
Potassium	105	79	186	418
Sodium	98	70	199	407
Calcium	104	64	152	354
Aluminium	56	24	129	265
Zinc	49	25	85	160
Lead	43	20	52	84
Hydrogen	41	−6	66	83
Copper (cuprous)	33	16	40	49
Silver	30	15	7	31
Gold (aurous)	10	2	—	—

Intrinsic or Internal Energy —We may define the internal energy content as follows: *Every substance under given external conditions contains a definite quantity of energy associated with it and this amount of energy is called* the internal or intrinsic energy *of the substance.*

Now, consider the equation, C + 2H₂ = CH₄ + 18,800 cals. Since the principle of conservation of energy holds good, we may

regard that one mol of methane contains 18,800 cals less energy than the total amount of internal energy contained in one mol of carbon and two mols of hydrogen. So, a thermochemical measurement gives only the *difference* of internal energy between the original and the final system but not the *absolute* amount of energy of any of the systems. Unfortunately, the absolute amount of energy contained in any system is not known and we have no method to compare the total internal energy content of different elements. Evidently, the latter information is impossible to obtain, for we cannot convert carbon into oxygen or any element into any other.

But one certain fact comes out from the above equation : whatever may be the values for the intrinsic energies of carbon and hydrogen, the intrinsic energy of methane is less than their sum total of energy by 18,800 cals. We can therefore assign any arbitrary value for the intrinsic energy of the elements, and refer the intrinsic energy of compounds to this value for the elements. *The most convenient system is to fix the intrinsic energy of all elements to be equal to zero.* The intrinsic energy of methane then comes out to be equal to −18,800 cals. meaning thereby that a mol of methane contains 18,800 calories *less* energy than its elements. Therefore, according to this convention the *intrinsic energies of all substances become just the negative of their heats of formation.*

or, **Intrinsic Energy = − Heat of Formation**   ...   (1)-IX

Hence intrinsic energy does not mean the absolute amount of energy contained in the substance but only the energy content of the substance in excess of that of its component elements. This convention is evidently *not applicable* to elements exhibiting *allotropy.* For example, during the formation of one mol of ozone from oxygen 29,600 cals are absorbed ; so, if the intrinsic energy of oxygen be zero, that of ozone is 29,600 cals. In the transformation of graphite to diamond 490 cals. are absorbed ; so, diamond has a greater intrinsic energy than graphite. In such cases, the intrinsic energy of the naturally occurring or stabler modification is usually taken to be zero and other modifications are referred to this standard.

The student should note that the above relation is simply a restatement of the equation already deduced (*vide* Ch. VII, P. 95 & 96) viz. $\triangle E = -$ *heat of reaction at constant volume*, or $\triangle H = -$ *heat of reaction at constant pressure*, and so it involves no new principle.

Importance of Intrinsic Energy Values or Heats of Formation in Solving Numerical Problems —The above convention makes the calculation of heat of formation and heat of reaction very easy. According to the law of conservation of energy, if the intrinsic energies of substances taking part in a chemical reaction be substituted in a thermochemical equation the equality will still

hold good. For example, if in the equation, $A + B = C + D + Q$ cals., we substitute the intrinsic energies (*i.e.* the negative of the heats of formation) of A, B, C and D, we can immediately calculate Q, the heat of reaction. Some illustrative calculations are shown below.

Example 2. *Calculate the heat of formation of carbon disulphide given that the heats of combustion of carbon disulphide, sulphur and carbon are 265,100 cal., 71,080 cals. and 94,300 respectively.*

$$CS_2 + 3O_2 = CO_2 + 2SO_2 + 265,100 \text{ cals.} \quad \text{...} \quad \text{...} \quad (i)$$
$$S + O_2 = SO_2 + 71,080 \text{ cals.} \quad \text{...} \quad \text{...} \quad (ii)$$
$$C + O_2 = CO_2 + 94,300 \text{ cals.} \quad \text{...} \quad \text{...} \quad (iii)$$
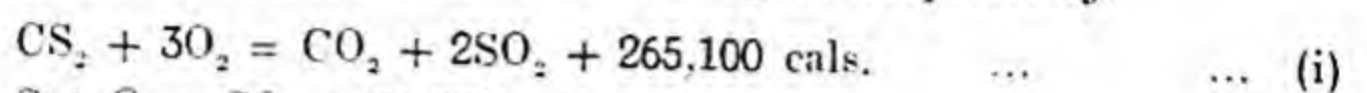
From equation (ii) and (iii) it follows that the intrinsic energies of SO_2 and CO_2 are—71,080 and—94,300 calories respectively. Let the intrinsic energy of CS_2 be E_{CS_2}. Substituting these values of intrinsic energies in equation (i) we get—

$$E_{CS_2} + 0 = -94,300 + 2 \times (-71,080 + 265,100 \text{ cals.}$$

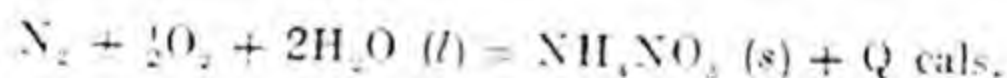$$\therefore \quad E_{CS_2} = 28,640 \text{ cals.}$$

$\therefore$ Heat of formation = – Intrinsic energy = – E_{CS_2} = –28,640 cals.

So, it is an endothermic compound.

Example 3. *Calculate how much heat will be liberated in the hypothetical reaction of synthesising ammonium nitrate from air and water, using data in table on P. 115.*

The equation in question is

$$N_2 + \tfrac{1}{2}O_2 + 2H_2O \; (l) = NH_4NO_3 \; (s) + Q \text{ cals.}$$

Now, $E_{N_2} = 0$, $E_{O_2} = 0$, $E_{H_2O} \; (l) = -68,400$, and $E_{NH_4NO_3} \; (s) = -88,000$. Substituting these values, we obtain, $Q = -48,800$ cals., *i.e.* the reaction takes place with an absorption of 48,800 calories.

Heat of Combustion—*It is the amount of heat evolved when one gram molecule of the substance is completely burnt down in oxygen.* Thus, the equation,

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O + 340,500 \text{ cals.}$$
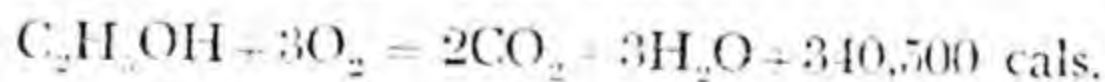
means that when one mol of alcohol is burnt in excess of oxygen 340,500 cals. of heat are evolved and the latter quantity is called the heat of combustion of alcohol. The combustion of a substance may take place either in a closed space (*i.e.* at constant volume), or in the open (*i.e.* at constant pressure). The former procedure is experimentally convenient but the results are more usually expressed after calculation at constant pressure and are explicitly mentioned to be so.

The heat of combustion is an important constant as it is a primary experimental data directly obtained from experiment, and also because many important heat changes, particularly in organic chemistry, are calculable from such data. The heats of combustion in K-cal/mol of a few representative organic compounds are given in the following table (25°C. 1 atm. H_2O (*l*)). Values in K-cal/lb. for a few food materials are also included.

Methane (CH$_4$)	212·8	Propyl alcohol	480·5
Ethane (C$_2$H$_6$)	372·8	Butyl alcohol	638·6
Propane (C$_3$H$_8$)	530·6	Glycerol	397·0
Butane (C$_4$H$_{10}$)	687·9	Cane Sugar	1349·6
Ethylene (C$_2$H$_2$)	337·3	Cereals, rice etc.	1650
Acetylene (C$_2$H$_2$)	342·0	Fats and oils	3650
Methyl alcohol	173·6	Milk, condensed	1500
Ethyl alcohol	326·7	Fish	1000

Application of Heat of Combustion Data—These basic thermochemical data find utility in various ways, a few of which are listed and discussed below.

(i) *Calorific value of fuels*

(ii) *Food value of diets*

(iii) *Maximum flame temperature*

(iv) *Calculation of heat of formation*

(v) *Calculation of heat of reaction.*

(i) & (ii) Calorific Value of Fuels and Food —Fuels, *e.g.*, coal, petroleum, etc. are to be assessed with respect to their calorific values with the help of heat of combustion data, and extensive measurements of the same for various fuels are made as a routine procedure for grading and standardising fuels.

Heat of combustion data are also useful for the science of food and nutrition. Foods taken are burnt inside the body, the energy liberated being used for keeping the body warm and for producing muscular energy. An average adult requires from 2000 to 3000 K-cal per day and so from heat of combustion data of foods some typical values for which are included in the table, it is possible to calculate the food requirement of the average individual, and hence of a nation. Of course, other considerations besides calories are required for securing a balanced wholesome diet which however need not concern us here. It may however be of interest to know that the average calorific value of food consumed in India per person per day is about only 1600 Cal whereas in western countries it is about 3000 Cal.

(iii) Maximum flame temperature—A very interesting application of the heat of combustion data is made in the calculation of the maximum *temperature of flames*. The principle of calculation is very simple, since one has to calculate from the known specific heats of the products of combustion their maximum rise in temperature at the expense of the heat of combustion of the gas responsible for the flame. For example, for hydrogen flame, the upper limit of temperature will be that to which an equal volume of water vapour mixed with the nitrogen of the air used up in the combustion can be raised by the heat of combustion of hydrogen.

EXAMPLE 4. *Calculate roughly the maximum temperature attainable with an oxy-hydrogen flame, given that the heat of formation of H$_2$O (g) is 57,800 cals, and the average molar heat of water vapour is 9·3 Cals./mol.*

8

We have to calculate to what temperature a mol. of water vapour will be raised by the heat of combustion. Now, rise of temperature = Heat evolved/specific heat $\times$ mol. wt. $\therefore$ Temp. rise = 57,800/9·3 = 6200°C. Of course, the actual temperature is much less owing to radiation loss, incomplete combustion and other factors.

(iv) Heat of reaction from heat of combustion—The principle of this method is that if we know the heats of combustion of all the reactants and resultants and substitute these values in the thermochemical equation, the equality still holds good just as if the intrinsic energies were substituted. That is, in a reaction $A+B=C+D+Q$ calories,

Heat of reaction, $Q = (a+b) - (c+d)$ ... ... (2)-IX

where a, b, c and d are the *heats of combustion of* A, B, C and D respectively (*vide* Ex. 5). This is a very convenient relation for working out sums.

EXAMPLE 5. *The heats of combustion of ethane, ethylene and hydrogen are 370,440 cal., 333,350 cals. and 68,400 cals. respectively. Calculate the heat evolved in the reduction of ethylene to ethane.*
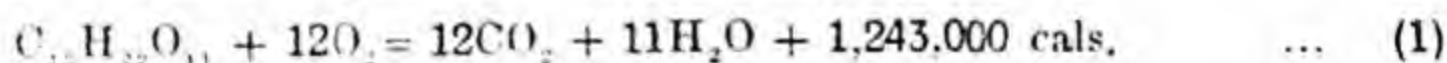
$$C_2H_4 + H_2 = C_2H_6 + Q \text{ cals.}$$

Substituting the heats of combustion of ethylene, ethane and hydrogen, in the above equation we get—

$$333,350 + 68,400 = 370,440 + Q \text{ or, } Q = 31,310 \text{ calories.}$$

In adopting this method, it is advisable to explain the principle first of all. The ordinary methods, though more roundabout are of course applicable.

(v) Heat of formation from heat of combustion—Since heat of formation is after all a type of heat of reaction its value can be calculated by proper algebraic manipulation of heat of combustion equations. In fact many of the heat of formation data have been computed from combustion data. An illustrative example is shown below.

EXAMPLE 6. *The heat of combustion of cane sugar is 1,243,000 cals, and those of hydrogen and carbon are 68,360 and 94,800 calories respectively. Calculate the heat of formation of cane sugar.*

$$C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O + 1,243.000 \text{ cals.} \quad ... \quad (1)$$
$$C + O_2 = CO_2 + 94,300 \text{ cals.} \quad ... \quad ... \quad ... \quad (2)$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68,360 \text{ cals.} \quad ... \quad ... \quad ... \quad (3)$$

From eqn. (2) and (3) it follows that the intrinsic energies of CO_2 and H_2O are—94,300 and—68,360 cals. respectively. Substituting these values of intrinsic energies in eqn. (1) and putting the intrinsic energy of sugar equal to E_{SUGAR}, we have,

$$E_{SUGAR} + 0 = 12 \times (-94,300) + 11 \times (-68,360) + 1243,000 \text{ cals.}$$

Or, $E_{SUGAR} = -640,560$ calories. But, heat of formation $= -E$

Therefore, the heat of formation of cane sugar is 640,560 cals.

Experimental Determination of Heats of Combustion—The apparatus in general use for this purpose is Berthellot's Bomb Calorimeter, a sketch figure of which is given (Fig. 41). The apparatus consists of a strong vessel T fitted with a *screw-on lid*. The vessel is made of steel which is coated inside with some

non-oxidisable metal such as gold or platinum. Through the lid passes *two insulated platinum wires* (p. p.) which are connected by a *spiral* of thin *iron wire*. Through the lid there is a valve through which oxygen is pumped in so as to reach a pressure of nearabout 25 atmospheres. The spiral of iron wire is placed in contact with a weighed quantity of the substance contained in the *platinum capsule*, C. The whole is immersed in a calorimeter filled with water and the combustion is started by sending a *current* through the iron wire. The iron wire burns out and the molten product falls in the capsule on the substance (if liquid, contained in a thin sealed glass bulb) and ignites it so that it may completely burn out in the excess oxygen. From the rise in temperature of the water in the calorimeter, the amount of heat developed in the bomb is calculated in the usual way and therefrom making

Fig. 41
Bomb Calorimeter

a proper allowance for the heat developed by the combustion of the iron wire, the heat of combustion of the substance is calculated. Of course, all the usual precautions of calorimetry are taken.
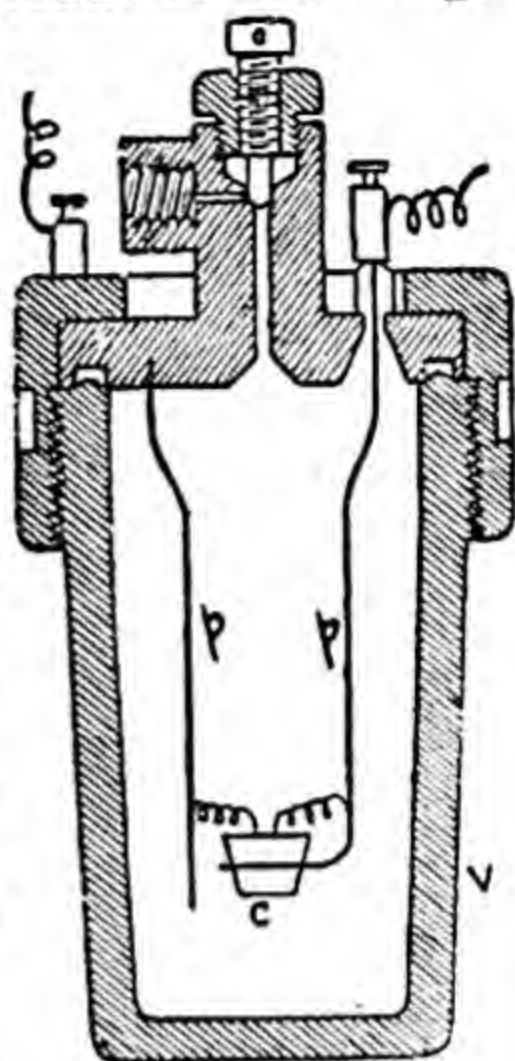
The method is applicable to all substances which burn completely in a well defined manner. Halogenated organic compounds give poor results because the products of oxidation are variable, and so they are not amenable to this method.

Empirical Thermochemical Calculations. Bond energy— It becomes often necessary to know a certain heat of reaction which it is not possible to calculate from available heat of formation data. In such cases various empirical methods are used to compute the necessary value. In the case of organic compounds a few empirical rules of a fair degree of accuracy but of limited applicability are available. For example, Thornton's rule that the heat of combustion of a hydrocarbon can be expressed as the sum of 105,920 cal. for each C (107,160 for aromatic C) and 52,420 cal. for each pair of hydrogen (51,780 for aromatic) is a fairly accurate one for hydrocarbons but like similar other rules is much in error for other compounds.

A more general approach to the problem has been made by Pauling who has found it possible to attribute the total energy of a molecule to the sum total of the energy of the chemical bonds present in the molecule. For example, the energy of the methane molecule may be considered to reside in the four C–H bonds and that of say ethylene in the C=C bond and four C–H bonds. In any chemical reaction some bonds are broken and new ones are formed and the heat of reaction is the algebraic

sum of the bond energies involved. For example, in the reaction $C_2H_4 + H_2 = C_2H_6$, the heat of reaction is simply the sum of six C–H bond energies added to one C–C bond energy, minus four C–H bond energy, one C=C bond energy and one H–H bond energy. The calculated value from bond energy table of the above reaction is 29 K-cal, whereas the observed value is 32·7 K-cal. Some values of bond energy in K-cal are:—C–C=58·6, H–H=103·4, C–H 87·3, C=C=100, O–H=110·2, C=O (alde-hydes)=149, C=O (ketones) =152, etc. Calculations based on bond energy are fairly satisfactory, provided there is no resonance in the molecule and in the event of the existence of the latter a correction for resonance energy has to be made (for discussion on resonance, *vide* Ch. XXVII).

DEPENDENCE OF HEAT OF REACTION ON EXTERNAL CONDITIONS

(a) Influence of External Pressure— *Heat of Reaction at Constant Volume (Q_v) and at Constant Pressure (Q_p)*: If the number of gaseous molecules formed by a chemical reaction is different from that present originally, the pressure of the system would change if it is maintained at a constant volume, or the volume of the system would change if the external pressure is kept constant throughout. The heat evolved when the system is maintained at constant pressure is called the *heat of reaction at constant pressure* (symbolised, Q_p) and is different from the *heat of reaction at constant volume* (symbolised, Q_v).

In case the *number* of gaseous molecules *increases* due to the chemical reaction (*e.g.* $N_2O_4 = 2NO_2$), increase of volume takes place if the pressure is maintained constant. The work done by this increment of volume is to be supplied at the cost of the energy of the system itself and so, the heat evolved at constant pressure Q_p is less than that liberated at constant volume Q_v.

On the other hand when the *number* of mols *decreases* due to the reaction (*e.g.* $2H_2 + O_2 = 2H_2O$), the system contracts in volume and so, work is done upon the system which is liberated as heat ; therefore, Q_p becomes *greater than* Q_v.

In case there is no change of volume due to the equality in the number of gaseous molecules on both sides of the equation (*e.g.* $H_2 + Cl_2 = 2HCl$), Q_p and Q_v have one and the same value.

If n mols of gas are produced in the reaction the external work done by the gas is nRT (since work = pressure × volume = $PV = nRT$). Therefore, the actual relation embracing both the cases becomes,

$$Q_p = Q_v - (n_2 - n_1)RT = Q_v - \triangle nRT \qquad \ldots \qquad \ldots \text{(3)-IX}$$

where n_2 = number of moles of *products* and n_1 = number of mols of *reactants* and therefore, $\triangle n = n_2 - n_1 = net$ *increase* in the number of mols of gaseous substance, and R has a value of

2 calories. So, when $\triangle n$ is positive (*i.e.* the number of gaseous molecules increases by the reaction), Q_p is less than Q_v; and when $\triangle n$ is negative (*i.e.* the number of gaseous mols decreases) Q_p is greater than Q_v.

EXAMPLE 7. *The heat of formation of methane at constant pressure is 18,500 cals. at 25°C. Calculate the heat of reaction at constant volume.*

$C + 2H_2 = CH_4 + 18,500$ calories.
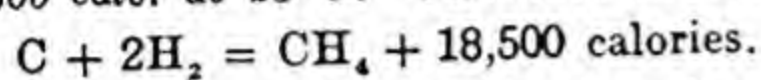
Given $Q_p = 18,500$ cals., $R = 2$ cals.; $T = 298°$ Abs.

$n_1 =$ mols. of gaseous reactants $= 2$; $n_2 =$ mols. of gaseous products $= 1$.

$\therefore \quad \triangle n =$ net increase in mols $= n_2 - n_1 = 1 - 2 = -1$.

Substituting in the equation, $Q_p = Q_v - \triangle nRT$, we get

$Q_v = 18,500 + (-1) \times 2 \times 298 = 17,904$ calories.

Alternative Thermodynamic Derivation —The above equation (3-IX) can be easily deduced from thermodynamics. By definition of the heat content, H we have

$$H = E + PV = E + nRT$$

Taking difference between the final and the initial state and indicating it by $\triangle$, we have

$$\triangle H = \triangle E + \triangle nRT$$

But $\triangle H = -Q_p$ and $\triangle E = -Qv$ and so we get

$$Q_p = Q_v - \triangle nRT$$

(b) Temperature Dependence of Heat of Reaction—The thermochemical principles have an interesting application in the calculation of the heat effect of the same reaction at different temperatures. Consider, for definiteness, a specific reaction such as $Pb + \frac{1}{2}O_2 = PbO$ occurring at constant pressure at two temperatures T_1 and T_2 evolving Q_1 and Q_2 calories of heat respectively. Now, starting from lead and oxygen at the lower temperature T_1, we can obtain lead oxide at the temperature T_2 in two ways. We may either allow the reaction to take place at temp. T_1 to obtain PbO at the same temp. and then heat this up to the temperature T_2. The net heat *evolved* in the process is $Q_1 - C_p^* (T_2 - T_1)$, where C_p^* is the average molar heat capacity of litharge and the term $C_p^* (T_2 - T_2)$ is the heat necessary for the final heating.

On the other hand we may first heat up the mixture of Pb and $\frac{1}{2}O_2$ to the temperature T_2 and then allow them to react to produce litharge at this higher temperature evolving Q_2 calories.

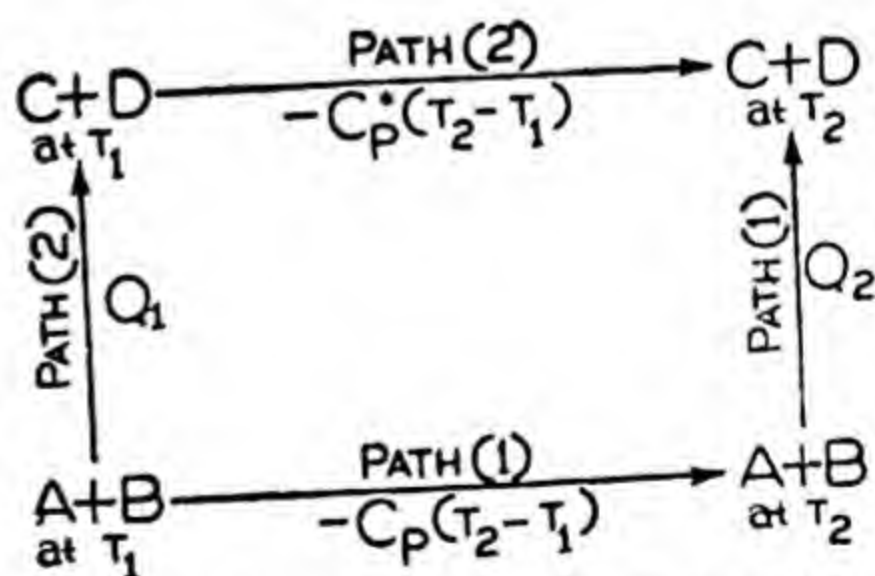Fig. 42—Diagrammatic Representation of Kirchoff's equation.

The net heat evolved is

$Q_2 - C_p(T_2 - T_1)$ where C_p is the heat capacities of the reactants i.e. $Pb + \frac{1}{2}O_2$.

Now, since the final and the initial stages are the same in both the above cases, the thermal effects must be equal by Hess's law or the law of conservation of energy, i.e.,

$$Q_2 - C_p(T_2 - T_1) = Q_1 - C_p^*(T_2 - T_1)$$

Or $Q_2 - Q_1 = (C_p - C_p^*)(T_2 - T_1) = -\Delta C_p(T_2 - T_1)$ ... (4)-IX

where ΔC_p means increase in heat capacity of the system. This equation is called *Kirchoff's equation.*

Alternative Derivation of Kirchoff's Equation— The above equation can be very simply derived from the thermodynamic definition of specific heat. The equation for constant pressure (*vide* Ch. VIII, P. 100) is,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \text{ or } \Delta C_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p$$

$\therefore$ At constant pressure, $d\Delta H = \Delta C_p dT$

Integrating both sides within limits, and considering ΔC_p independent of temperature, we get

$$(\Delta H)_2 - (\Delta H)_1 = \Delta C_p(T_2 - T_1) \qquad ... \qquad ... \quad (5)\text{-IX}$$

which is the Kirchoff's equation. This equation becomes the same as our previous equation, if we substitute $\Delta H = -Q_p$ since ΔH is the negative of the heat of reaction at constant pressure.

EXAMPLE 8. *The latent heat of evaporation of water at 100° at constant pressure is 538 cal/gm. If average C_p for water and steam are 1 cal/gm. and 8·1 cal/mol respectively for the interval, calculate the latent heat of water at 150°C.*

Here, the reaction is formally, water=steam. We have per gm basis, $(\Delta H)_{150} = ?$; $(\Delta H)_{100} = 538$; C_p for water $= 1$; C_p for steam $= 8\cdot1/18$; $\Delta C_p = 0\cdot45 - 1 = -\cdot55$ and $T_2 - T_1 = 150 - 100 = 50$. Substituting in equation (4), we get, $(\Delta H)_{150} - 538 = -0\cdot55 \times 50$; or, $(\Delta H)_{150} = 510\cdot5$ cal/gm. i.e. latent heat of evaporation of water at 150°C is 510·5 calories/gm.

EXAMPLE 9. *The heat of formation of PbO is 52,460 calories at 18°C; calculate the same at 300°C, given that the mean specific heats of lead, oxygen and litharge in this range are 0·032, 0·215 and 0·052 respectively.*

Now, $Q_1 = 52,460$ calories; for $Pb + \frac{1}{2}O_2 = PbO$

$C_p^* = $ molar heat of litharge = mol. wt. $\times$ sp. heat $= 223 \times 0\cdot052 = 11\cdot6$.

$C_p = $ atomic wt. of Pb $\times$ sp. heat $+ \frac{1}{2} \times$ mol. wt. of oxygen $\times$ sp. heat $= 207 \times 0\cdot032 + 16 \times 0\cdot215 = 10\cdot06$
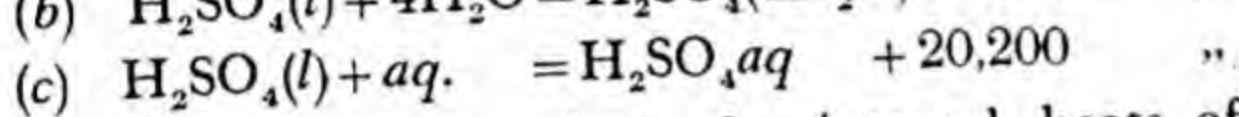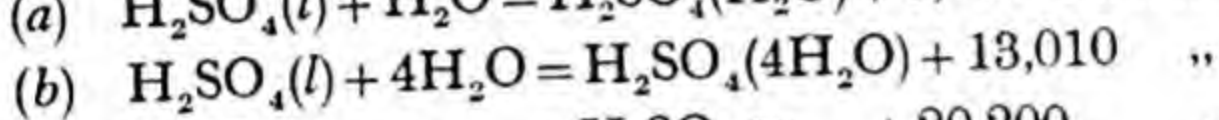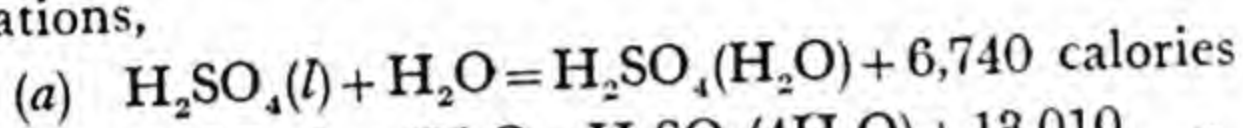
$\therefore \Delta C_p = C_p^* - C_p = 11\cdot6 - 10\cdot06 = 1\cdot54$.

Substituting in the equation, $Q_2 - Q_1 = -\Delta C_p(T_2 - T_1)$, we have $Q_2 = 52,460 - 1\cdot54(300 - 18) = 52,026$ calories.

Heat of Solution— *Heat of solution* may be defined as the amount of heat evolved when one gram molecule of a solute is

dissolved in sufficient amount of a solvent so that on further dilution no more thermal effects are observed. For example, on addition of 250 c.c. water to one mol hydrochloric acid gas 16,500 calories are evolved; addition of another 250 c.c. water liberates 450 calories; a further addition of 500 c.c. water gives out another 300 calories; dilution with 1 litre more water yields 150 cals more and on further addition of water no more heat effect is observed. So the heat of solution of hydrochloric acid is $16,500 + 450 + 300 + 150 = 17,400$ calories.

Very often however in modern thermochemical literature the heat of solution data are given for a specified amount of water added and such heats of solution are called *integral heat of solution*. For example, in the following thermochemical equations,

(a) $H_2SO_4(l) + H_2O = H_2SO_4(H_2O) + 6,740$ calories
(b) $H_2SO_4(l) + 4H_2O = H_2SO_4(4H_2O) + 13,010$,,
(c) $H_2SO_4(l) + aq. = H_2SO_4 aq + 20,200$,,

The first two equations show the integral heats of solution of sulphuric acid in specified amounts of water, whereas the last equation shows the total heat of solution. Hence the total heat of solution is the integral *i.e.* total heat of solution for infinite dilution.

A further point of interest is that the difference between two integral heats of solution gives the heat of dilution from the first solution to the final solution. Thus if we subtract equation (a) from equation (c) we get

$$H_2SO_4(H_2O) + aq. = H_2SO_4 aq. + 13,460 \text{ cal.}$$
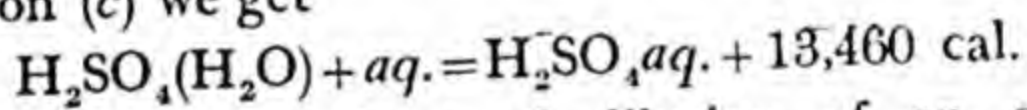
which means that the heat of dilution of an equimolecular mixture of water and sulphuric acid to infinite dilution is 13,460 calories.

Many substances, viz. ammonium salts, potassium salts, etc. dissolve in water with absorption of heat (*i.e.* the heat of solution is *negative*), and sometimes the absorption is so large as almost to reach the freezing point of water, but most substances dissolve in water with evolution of heat. When NH_4Cl dissolves in conc. HCl so much heat is absorbed that frost deposits on all sides of the containing beaker. Evidently, the heat of formation in solution is not the same as the heat of formation of the solid substance and is equal to the algebraic sum of the heat of formation of the substance and its heat of solution.

An interesting corollary of Le Chatelier principle (to be discussed later) may be pointed out in this connection. If a salt dissolves in a nearly saturated solution with evolution of heat, the solubility of the salt would decrease with increasing temperature, and on the other hand, if the heat of solution be negative, the solubility increases with rising temperature. In fact it is possible to calculate the heat of solution (in a nearly

saturated solution) of a salt from the temperature coefficient of solubility and *vice versa*.

Heat of Reaction of other Types—Besides the types of heat of reaction mentioned so far there are various other heats of reaction, to name a few, heat of hydrogenation, heat of dissociation, heat of hydration, heat of crystallisation, heat of sublimation, heat of transition, etc. Meaning of all these heats is apparent from the names themselves as they simply refer to the heat liberated in a particular types of reaction or process. However, they need no special consideration as they are subject to the same type of laws and treatment as given to the other heats in this chapter.

Thermochemistry of Solution—Two very interesting results were obtained from a study of the heat effects in solution. The first result is known as the *law of thermoneutrality of salt solutions*, which states that when two dilute solutions of inorganic salts are mixed, heat is neither evolved nor absorbed, provided no precipitation takes place. The second result of importance is that *the heat of neutralisation of a strong acid by a strong base is approximately constant and is equal to 13,800 calories*.

The above results become easily intelligible in the light of the theory of electrolytic dissociation. When two salt solutions say, $NaCl$ and KNO_3 are mixed, no reaction takes place but the mixture contains all the four ions Na^+, Cl^-, K^+ and NO_3^-, present side by side in the solution. Since the salt solutions are almost completely dissociated, the net reaction is represented by

$$(Na^+ + Cl^-) + (K^+ + NO_3^-) = Na^+ + Cl^- + K^+ + NO_3^-$$
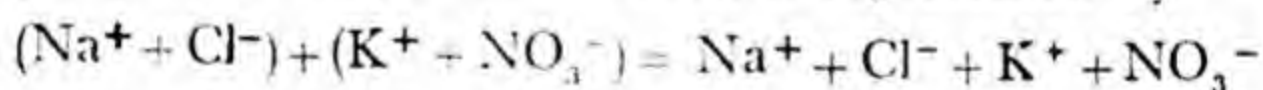
which indicates practically no reaction at all and so does not evolve any heat. In case precipitation takes place on mixing dilute salt solutions (for example, lead nitrate and potassium iodide), heat effects are usually observed. It can be easily shown that the heat of mixing in such a case is substantially equal, but opposite in sign, to the heat of solution of the precipitated substance (e.g. lead iodide).

Heat of Neutralisation—The constancy of the heat of neutralisation of all strong acids and bases, mentioned in the previous section, can be easily explained. According to the ionic theory, in the neutralisation of strong acids and bases, the net reaction is the combination of H^+ and OH^- ions to form water as represented below—

$$(Na^+ + OH^-) + (H^+ + Cl^-) = Na^+ + Cl^- + H_2O.$$
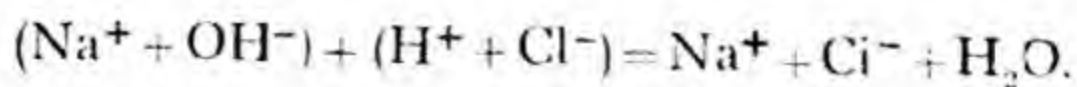
Therefore, the observed heat of neutralisation is the heat of reaction of $H^+ + OH^- = H_2O$, which is equal to 13,800 calories. The heats of neutralisation of some common acids and basis are shown in the accompanying table.

Acid	Alkali	Heat of neutralisation
HCl	LiOH	13,700 cals.
HCl	NaOH	13,680 ,,
HCl	KOH	13,930 ,,
HNO$_3$	NaOH	13,690 ,,
HCl	NH$_4$OH	12,500 ,,
CH$_3$COOH	NaOH	13,300 ,,
CH$_3$COOH	NH$_4$OH	11,900 ,,
$\frac{1}{2}$ H$_2$S	NaOH	3,800 ,,
$\frac{1}{2}$ H$_2$S	NH$_4$OH	3,100 ,,
HCN	NaOH	2,900 ,,
HCN	NH$_4$OH	1,300 ,,
HF	NaOH	16,400 ,,

However, if either or both the acid and the base be weak, the heat of neutralisation will not be equal to 13,800 calories. Suppose we neutralise a very weak acid say, hydrocyanic acid with caustic soda in solution. This process is found to evolve only 2,900 calories. The hydrocyanic acid will be practically undissociated and so we can represent the neutralisation in two steps, the ionisation of HCN followed by its neutralisation as shown below—

$$HCN = H^+ + CN^- + q$$

$$H^+ + CN^- + Na^+ + OH^- = Na^+ + CN^- + H_2O + 13,800 \text{ cal.}$$
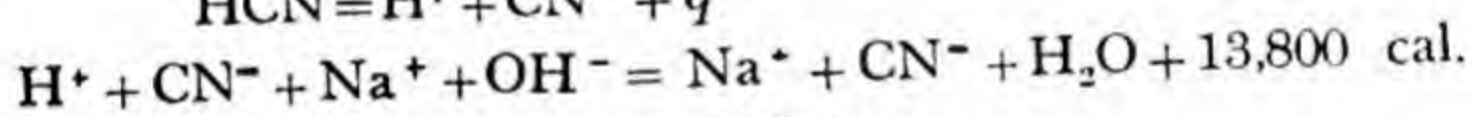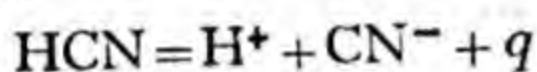
Adding the two equations we have

$$HCN + Na^+ + OH^- = Na^+ + CN^- + H_2O + (13,800 + q) \text{ cal.}$$

Since q, the heat of ionisation is generally negative the observed heat of neutralisation for weak acids and bases will be less than that for strong acids and bases i.e. 13,800 calories. Hence, we conclude that 10,900 calories (13,800 − 2,900 = 10,900) are necessary for the ionisation of one mol of HCN.

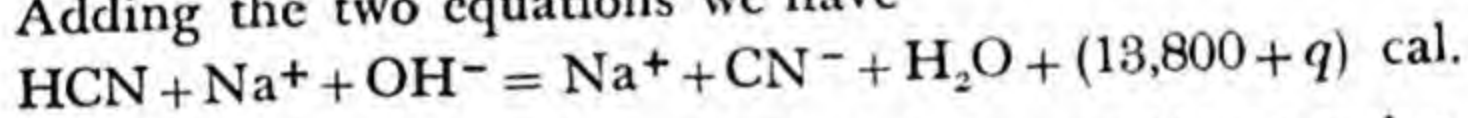CHEMICAL AFFINITY AND HEAT OF REACTION (STABILITY OF COMPOUNDS)— For more than a century chemists sought in vain for a numerical measure of chemical affinity. It was observed that reactions which are strongly exothermic, take place with gerat ease and rapidity forming very stable products. Accordingly, Berthellot and Thomsen identified the heat of reaction as a measure of chemical affinity; in other words the larger the amount of heat evolved during the formation of a compound, the stronger will be the affinity between the component atoms i.e. the substance will be more stable.

Two very simple objections can show the inadequacy of this principle. Firstly, the above rule cannot explain the formation of stable endothermic compounds and secondly, it ignores the fact that most reactions are reversible and so, can go both ways. In fact, the heat of formation is in no way a measure of the stability of a compound, though in most cases an approximate parallelism is noted.

It has been shown on thermodynamic grounds that every spontaneous reaction, if suitably conducted, can be made to yield some external work. The maximum value of this external work at constant temperature and pressure which is called the *free energy change*, $\triangle$F of a reaction is a

tion of CO_2 and H_2O are 91,300 cal. and 68,300 cal. respectively. Calculate the heat of formation of methane.   [17,100 cal.]

13. In nature calcium carbonate occurs as calcite and aragonite. Suggest a method for determining the heat of transition, the direct transition being too slow to be measured.

14. What is the relation between heat of reaction at constant volume and at constant pressure. The heats of combustion at constant volume of carbon, carbon monoxide, hydrogen and methyl alcohol (l) at 200°C are 97,000 cal., 67,700 cal., 68,400 cal. and 170,600 cal. respectively. Calculate the corresponding heats of combustion at constant pressure.

$$(a = 97,000; \quad b = 68,173; \quad c = 68,873; \quad d = 169,181.)$$

15. From the following data at constant volume at 17°C, calculate the heat evolved in the conversion of acetylene to benzene (a) at constant volume and (b) at constant pressure.   [Hint : use eqn. (2)-IX].

(i) $C + O_2 = CO_2 + 96,960$ cal.

(ii) $2H_2 + O_2 = 2H_2O$ (liquid) $+ 1,36,720$ cal.

(iii) $C_6H_6 + 15O_2 = 12CO_2 + 6H_2O$ (liquid) $+ 1,58,700$ cal.,

(iv) $2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$ (liquid) $+ 620,100$ cal.,

$$[Q_V = 130,800 \text{ cals.}; \quad Q_p = 131,960 \text{ cals.}]$$

16. What do you understand by the terms "heat of reaction", "heat of formation" and "thermochemical equations"? What is the relation between heat of reaction at constant pressure and heat of reaction at constant volume? Illustrate with an example how the heat of reaction is determined indirectly.

17. A solution of the composition $CuCl_2 + 10H_2O$ is diluted with 'b' molecules of water. The heat disengaged in this dilution is expressed by the empirical formula, $Q_V = \dfrac{b \times 5023}{b + 21 \cdot 24}$ The heat of solution of $CuCl_2$ in 600 mols of water is $Q_1 = 11,080$ cals. Find out the heat of solution of anhydrous $CuCl_2$ in 10 moles of water and find out the heat disengaged in the dilution of $CuCl_2 + 600$ aq. the dilution being effected till there is no more thermal change.   [6,231·6; 174·6]

Hint :—Put $b = 590$ in the equation to get heat of dilution of $CuCl_2 = 10H_2O$ to $CuCl_2 + 600H_2O$; again, put $b =$ infinity in the equation after dividing the numerator and denominator with b, whence we get the total heat of dilution of $CuCl_2 + 10H_2O$ to be 5023.

18. The heat of reaction $CO + \frac{1}{2}O_2 = CO_2$ is 57,600 calories at 18°C. Calculate the heat of combustion of carbon monoxide at 1000°C, given that the mean molar heats of CO, O_2 and CO_2 are 6·55, 6·5 and 10·5 respectively   [56,913]

19. To convert water into steam at 100°C, 539 calories per gm are required. Calculate the latent heat of evaporation at 50°C, assuming C_p to be 8 for steam per mol and unity for water per gram. [566·8 cals./gm.]

CHAPTER X

THE SECOND LAW OF THERMODYNAMICS

Introduction—While the first law (Ch. VIII) establishes the equivalence between heat and work it imposes no condition on their mutual convertibility. In other words, it never tells us under what circumstances and to what extent it is possible to convert one form of energy into another. Our experience however shows that there are some restrictions inherent in the nature of heat which limits its complete convertibility into work. For example, heat passes from a hot body to a cold body. First law tells us that the amount of heat lost by the hot body must be equivalent to that gained by the cold body but there is nothing in the first law which tells us that the heat has to flow spontaneously from the hotter to the colder body and not in the reverse direction. Taking another example, if we expand an ideal gas isothermally, the gas absorbs heat from the surroundings and converts it completely into work. If we could now take the gas back to its original condition without leaving any change in the surroundings, we could repeat the performance any number of times and thus could get an inexhaustible supply of work at the expense of the heat of the surroundings. There is nothing in the first law which tells the above process to be impossible because we are not creating energy, but, we are absorbing heat from the surroundings and are completely converting it into work. Our experience tells us however that this is impossible. Hence, there must be some other law besides the first law, which governs the direction of flow of heat and the extent of its convertibility into work. And, this law is the second law of thermodynamics.

Statement of the Second Law— The second law has been stated in various ways ; Clausius has stated it as follows: "*It is impossible for a self-acting machine unaided by any external agency to convey heat from a lower to a higher temperature.*" Some other different statements though essentially the same have been made of which that by Planck deserves special mention as it is very direct and definite. His statement in essence is that *it is impossible to lift a weight and cool a body without leaving any other change.*

In other words, however ingeniously we might construct a machine it is impossible to transfer heat from a lower temperature to a higher temperature, or to cool a body and completely convert this heat into work without leaving any other compensatory change. This is not due to any mechanical defect in our machine, but is owing to some property inherent in the nature of heat itself, which imposes some limitations on the direction of its flow and on the extent of its convertibility into work. Hence, a quantitative formulation of the second law would be to know

what *maximum* fraction of an amount of heat can be converted into work and what are its *minimum* compensatory changes. This can be best done with the help of an imaginary process, called Carnot Cycle which we shall do shortly.

Reversible and irreversible Changes—Consider a quantity of water enclosed in a vessel fitted with a weightless frictionless piston (Fig. 43). The pressure on the piston will be the saturation pressure of water at this temperature, say, P. If the pressure on the piston applied from outside is also P, the system is in equilibrium and no change will take place. Suppose the external pressure is increased by an infinitesimal amount to say, $P + dP$;
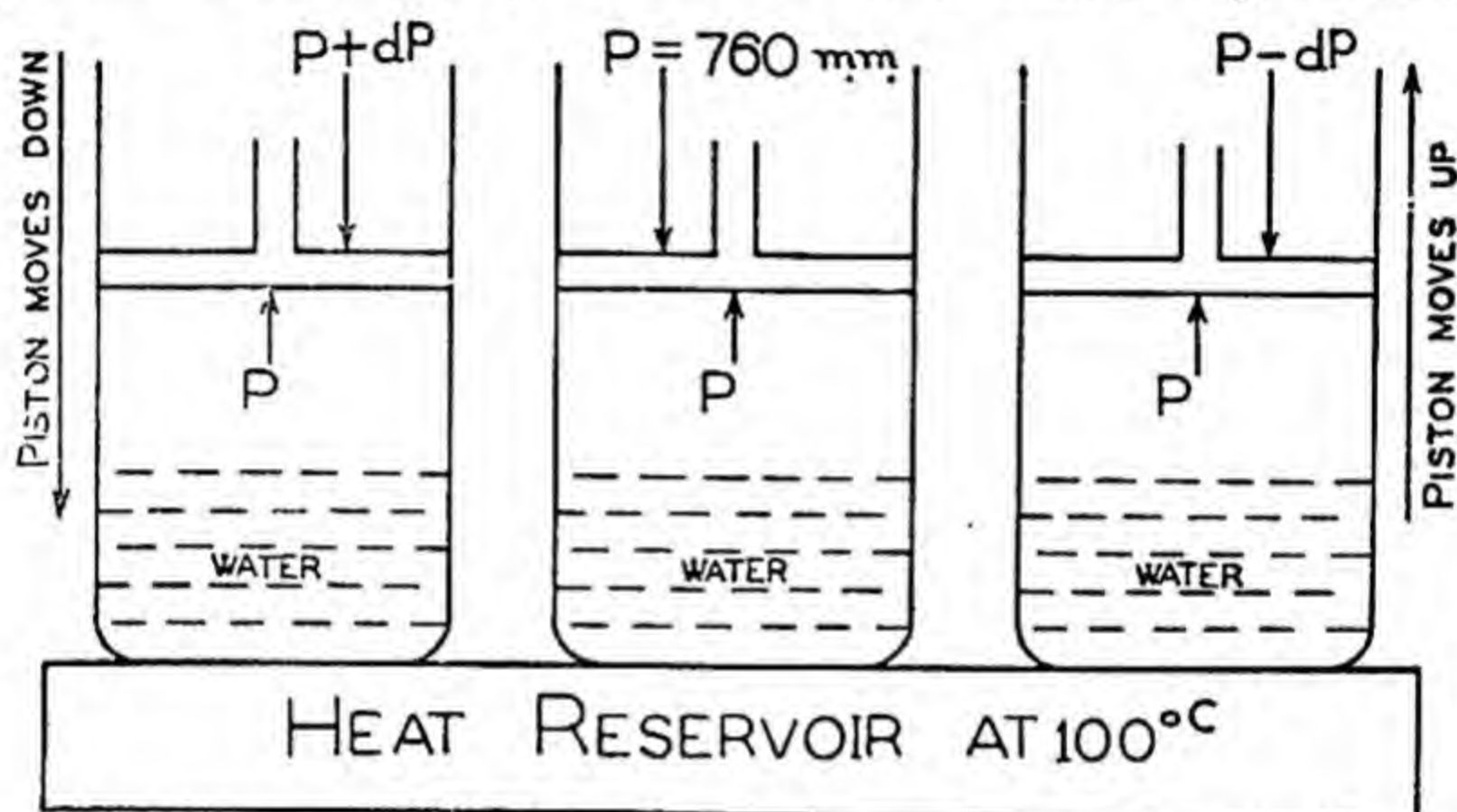
Fig. 43.—Reversible evaporation and condensation of a Liquid.

the piston will move down slowly until all the vapour is condensed into liquid. Similarly, if the external pressure is decreased by an infinitesimal amount say, to $P - dP$, the piston will slowly go up until all the water has been converted into vapour. The above two processes where the driving force is throughout infinitesimally greater than the opposing force are examples of reversible processes. Hence *any process whatsoever where the process can be made to go in both ways by just increasing or diminishing the applied force by an infinitesimal amount is called a reversible process.*

A very good example of a close approach to a reversible process is a galvanic cell, where if an external E.M.F. is applied to a cell such that it exactly balances the actual E.M.F. the cell reaction will come to a standstill, and the cell reaction can be made to run in either direction if the applied E.M.F. is either slightly more or slightly less than the true E.M.F. of the cell.

Alternative Definition of a Reversible Process—The concept of reversibility is fundamental to the science of thermodynamics and besides the foregoing definition of reversibility there are a number of other alternative definitions depending on the way

of looking at the process. An elegant definition depends upon the realisation that in a reversible process every intermediate stage is an equilibrium stage. We can therefore define a reversible process as one where all the intermediate stages are equilibrium stages, i.e., a reversible process proceeds along an equilibrium path.

There are two important points to be understood about reversibility. They are :—

(a) *A reversible process produces more work than the same process conducted irreversibly, and*

(b) *All natural processes, i.e. processes which take place spontaneously, are irreversible.*

The first point follows easily from the concept of work. If the applied force is less than the equilibrium pressure of the system, naturally, we are getting less work than the system is capable of yielding. For example, in the above illustration with water, suppose the water is at 100°C and so its vapour pressure is one atmosphere. If we apply a pressure which is almost equal to one atmosphere the piston will move up and will yield the maximum work. But if we apply a pressure which is perceptibly less than one atmosphere say, half an atmosphere, during the expansion the piston will go up against this pressure and we shall get only half the work for the same amount of water evaporated.

The second point follows from the fact that the reversible process is an infinitely slow process because the driving force is vanishingly small. But all actual processes go with measurable speed which means that there is a measurable difference between the driving force and the opposing force. Hence, such a process must be irreversible, the degree of irreversibility depending on the difference between the driving and the opposing force. When a stone slides along a hill the force and hence the work which we could have obtained by the fall of the stone is entirely lost. But suppose we could tie up this stone to some kind of spring which always applies a pull upwards just less than the pull of gravity. Eventually the stone will fall down to the earth though it will take an inordinately long time, and the whole energy of the stone will be found recovered and stored up as potential energy in the spring. In the unopposed fall *i.e.* in a natural process the energy of the fall is irrevocably lost.

Maximum Work during the Isothermal Reversible Expansion of a Perfect Gas—Having clarified the point that a reversible change produces more work than that obtainable from the same process conducted irreversibly, we might now calculate the maximum work obtainable by the *isothermal reversible* expansion of a *perfect* gas. If a gas has a pressure P_1 and the external pressure is reduced to $P_1 - dP$ where dP is infinitesimally small, the gas will expand to a volume $V + dV$ and its pressure will fall to $P_1 - dP$, when the gas will cease expanding.

The work done by the gas is $P_1 dV$. If now the pressure is reduced further to $P_1 - 2dP$, the gas will again do a little expansion by a very small volume dV, until its own pressure equals the external pressure, $P_1 - 2dP$. The work done in this stage is now equal to $(P_1 - dP)dV$. Such a process in which the applied pressure is always negligibly smaller than the gas pressure is to be continued on the gas until its pressure falls from the original pressure P_1 to the final pressure P_2 and the volume increases from V_1 to V_2. The above described process is a reversible process according to our previous definition and hence, yields the maximum work under the conditions. Therefore, the maximum work is just equal to the sum of all the small work terms like $P_1 dV$, $(P_1 - dP)dV$, etc. This summation can be easily done with the help of integral calculus as follows, for an expansion of volume from V_1 to V_2.
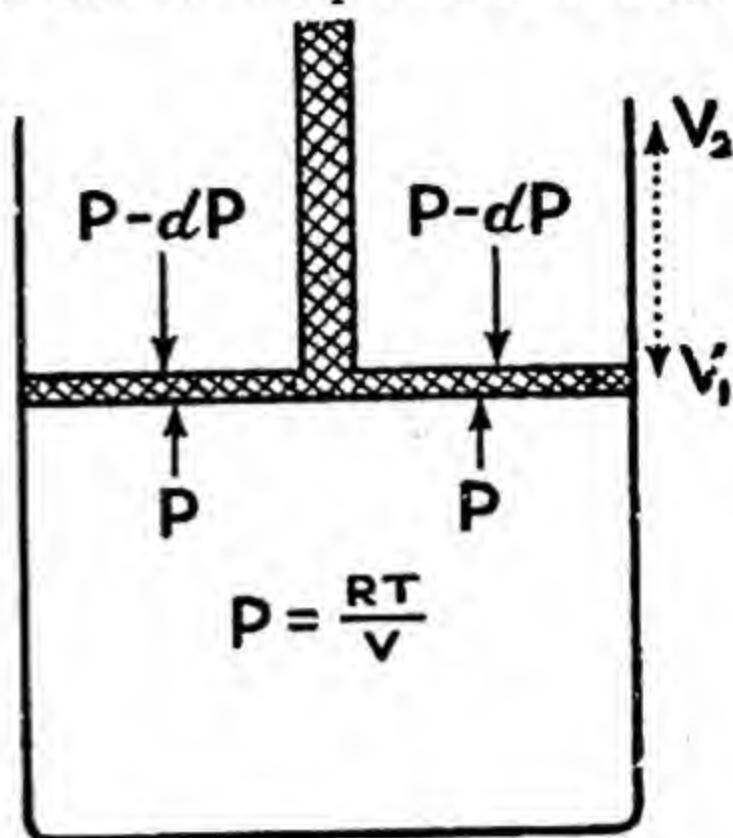
Fig. 44—Reversible isothermal expansion of a perfect gas.

$$\text{Maximum work} = P_1.dV + (P_1 - dP)dV + (P_1 - 2dP)dV$$

$$+ \ldots\ldots\ldots\ldots + (P_2 - dP)dV$$

$$= \int_{v_1}^{v_2} P.dV = \int_{v_1}^{v_2} \frac{RT}{V} dV$$

$$= RT \int_{v_1}^{v_2} \frac{dV}{V} = RT \ln V_2/V_1$$

Since at constant temperature $V_2/V_1 = P_1/P_2$.

$$\text{Maximum work} = RT \ln V_2/V_1 = RT \ln P_1/P_2 \qquad \ldots \quad (1)\text{-X}$$

So, the maximum work depends on the ratio of the two pressures and not on their absolute values. This rather surprising result is however, roughly corroborated by our experience of inflating bicycle tyres (which is of course a process far removed from reversibility), where we have noticed that the most strenuous part of the job is at the beginning and the finishing job is comparatively easier.

EXAMPLE 1. *Calculate the maximum work obtainable from the isothermal reversible expansion of a mol of perfect gas at 25°C from (a) 2 atm. to 1 atm., and (b) 10 atm. to 5 atm.*

(a) Max. Work = $2.303 \, RT \log P_1/P_2$

$= 2.303 \times (8.31 \times 10^7) \times 298 \, \log 2 = 1.66 \times 10^{10}$ ergs.

(b) Since $P_1 : P_2$ is the same, max. work is the same as (a).

This equation for maximum work in an isothermal reversible expansion of an ideal gas is important and will be often used. Note that when considering the reversible expansion of a vapour in contact with its liquid, we kept the applied pressure constant throughout because the pressure over a liquid does not change during the expansion of its vapour. In the above case, however, we had to continuously vary the applied pressure because the pressure of a gas falls during expansion according to Boyle's law. However, the indispensable condition of reversibility that the applied pressure must always be just smaller than the actual pressure was strictly adhered to in both the cases.
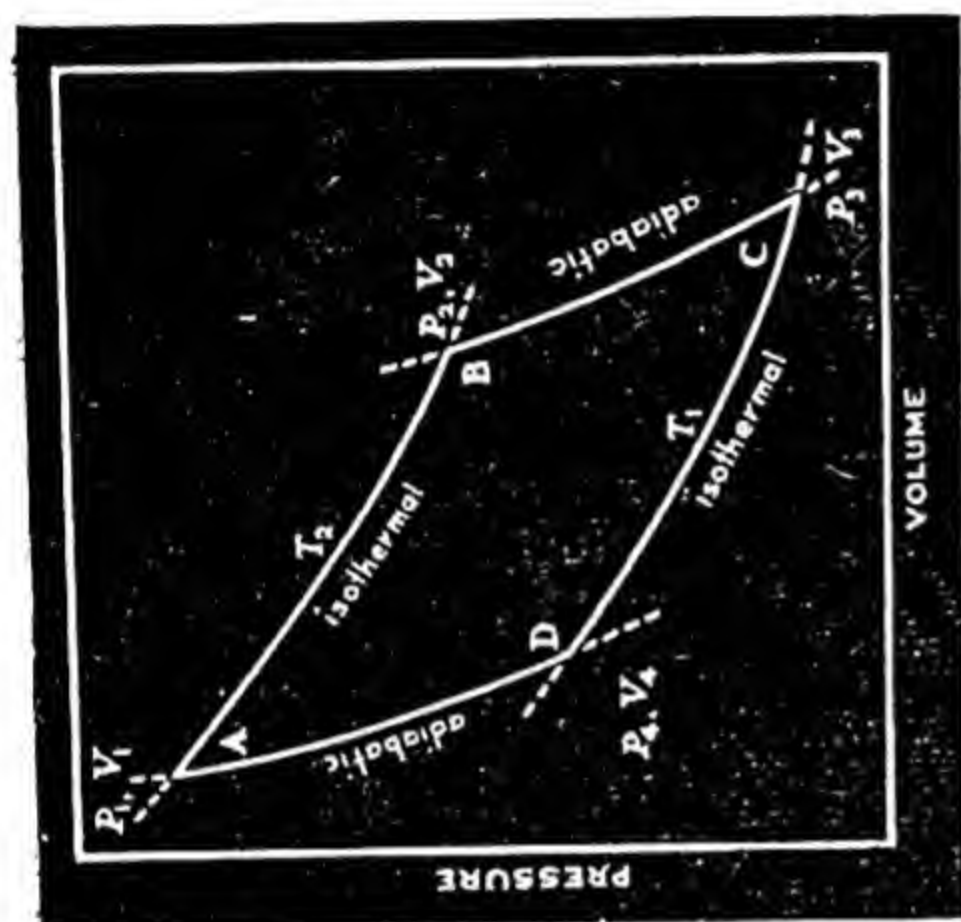
The Carnot Cycle— In order to find out the amount of work which is obtainable from a given quantity of heat, Carnot devised an imaginary cycle—a sequence of four operations on an ideal gas bringing it back to its original condition. Since the gas which is the working material in this imaginary engine is brought back to its original condition, its internal energy change is zero after the completion of the cycle, and so, by the first law (equation (4)-VIII), the algebraic sum of all the heat quantities absorbed by the gas during the cycle is equal to the algebraic sum of all the work done by the system. We now proceed to calculate the different heat terms and the different work terms in the various phases of the cycle.

Fig. 45—Carnot Cycle

We start with a mol of an ideal gas at a pressure P_1, volume V_1, and temperature T_2, confined in a cylinder fitted with a weightless frictionless piston and carry out the following four operations on it. (Fig. 45).

(a) *First Operation*—The gas is placed in contact with a large reservoir of heat at temperature T_2, and is expanded isothermally and reversibly along AB until its pressure and volume change to P_2 and V_2 respectively.

We already know that in this process the ideal gas absorbs heat from the surroundings (here the heat reservoir at temperature T_2) and does an equivalent amount of work given by equation (1). Let us call the work done in this first operation

9

w_1 and the heat absorbed q_2 (it is called q_2 to keep similarity with T_2).

Therefore, $w_1 = q_2 = RT_2 \ln \dfrac{V_2}{V_1}$ ... ... (a)

(b) *Second Operation*—The gas which is now at a pressure P_2, volume V_2 and temperature T_2 is isolated from any source of heat and further expanded adiabatically along BC to a pressure P_3 and volume V_3. We know that the temperature falls in an adiabatic expansion and let the new temperature be T_1. Since the process is adiabatic, $(q=0)$, we know (equation 11-VIII) that the work done at this second stage called w_2 is equal to the decrease in internal energy of the system.

$$w_2 = -\triangle E = C_v(T_2 - T_1) \qquad \ldots \qquad \ldots \text{ (b)}$$

(c) *Third Operation*—The gas, now at pressure P_3, volume V_3 and temperature T_1, is placed in contact with a heat reservoir at temperature T_1 and is compressed isothermally and reversibly along CD to meet the adiabatic curve passing through the point A *i.e.* to the point D. Let the new pressure be P_4 and volume be V_4. The compression is conducted isothermally and hence the temperature remains constant at T_1. During this compression along CD the gas gives out heat to the heat reservoir at T_1. Let this amount of heat be q_1. Also this amount of heat is equal to the work done *upon* the gas, called w_3, which is given by just the negative of the work done by the gas in the reverse process *i.e.* in the expansion along DC. Therefore,

$$w_3 = q_1 = RT_1 \ln \frac{V_3}{V_4} \qquad \ldots \qquad \ldots \qquad \ldots \text{ (c)}$$

(d) *Fourth Operation*—The gas is now thermally isolated and is compressed adiabatically along DE to come back to its original pressure, volume and temperature. As in the second stage, $q=0$ and the work done *upon* the gas during the adiabatic compression, is given by increase of internal energy.

$$w_4 = \triangle E = C_v(T_2 - T_1). \qquad \ldots \qquad \ldots \text{ (d)}$$

The gas is now back to its original condition *i.e.* it has undergone a complete cyclic operation and hence according to the first law the total work done by the gas is equal to the total heat absorbed by the gas. The total work done by the gas is equal to the work done by the gas during expansion in the first and the second stages minus the work done upon the gas during the compression in the third and the fourth stages : *i.e.*,

Total work, $w = w_1 + w_2 - w_3 - w_4$

Also, the total heat absorbed by the system is equal to the heat absorbed by the system at T_2 minus the heat given out at the temperature T_1 *i.e.*

Total heat absorbed $= q_2 - q_1$

Since, total heat absorbed = total work done, we have

$$q_2 - q_1 = w$$
$$= w_1 + w_2 - w_3 - w_4$$
$$= RT_2 ln V_2/V_1 + C_v(T_2 - T_1) - RT_1 ln V_3/V_4 - C_v(T_2 - T_1)$$
$$= RT_2 ln V_2/V_1 - RT_1 ln V_3/V_4 \qquad \dots \qquad \dots \qquad \dots \quad (e)$$

Also, we proved earlier (equation 22-VIII) that for any adiabatic

expansion, $VT^{C_v/R}$ = constant and therefore, for the two adiabatic curves, BC and AD, we have

$$V_2 T_2^{C_v/R} = V_3 T_1^{C_v/R} \text{ and } V_1 T_2^{C_v/R} = V_4 T_1^{C_v/R}$$

which on division gives $V_2/V_1 = V_3/V_4$.

Therefore, eqn. (e) becomes,

$$w = q_2 - q_1 = R(T_2 - T_1) \; ln \frac{V_2}{V_1}$$

Dividing this equation by equation (a), we get

$$\frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad \dots \qquad \dots \quad (2)\text{-X}$$

Now, q_2 is the heat absorbed at the higher temperature, T_2. w is the maximum work obtainable from the cycle and the term w/q_2 is the fraction of the heat which is converted into work. Hence, we come to an extremely important conclusion that *the maximum fraction of the heat which is convertible into work from a Carnot cycle depends only on the temperature of the two heat reservoirs and on nothing else.* The quantity w/q_2 is called the *thermodynamic efficiency* of the cycle and equation (2) may be regarded as a mathematical expression for the second law.

From the above equation for the efficiency of a Carnot cycle or any reversible cycle whatsoever, the interesting fact emerges that heat energy at higher temperature is more precious than heat energy at lower temperature because more of the former can be converted into useful work. So, in the sense of convertibility to work, heat and work are not completely equivalent, and they can be regarded as completely equivalent only at an infinitely high temperature.

Generality of the Equation of Carnot Cycle—We have derived the above expression for the efficiency of a Carnot cycle. Its importance however comes from the fact that it is also true for any other cycle using any material we like, provided we carry out the operations reversibly between the temperature limits, T_2 and T_1. The proof of this is very simple. Suppose we have a reversible engine working between the two temperatures T_2 and T_1 and having a higher efficiency than the Carnot engine. We can immediately couple the two engines so that the new engine runs directly and the Carnot's one runs in a reverse way, which

latter is possible because these engines are completely reversible. If we now adjust matter such that the heat given by the new engine to the low temperature reservoir is exactly taken up by the Carnot engine in its reverse operation, we shall have ultimately created a combination of engines which is continuously converting heat into work without leaving any other change. This latter process is impossible according to the second law. Hence, *any reversible engine whatsoever has the same efficiency as the Carnot engine*, provided the temperature limits are the same.

It is natural for the student now to raise the question what happens if we do not carry out a change as prescribed by Carnot, *i.e.* by a series of isothermal and adiabatic changes. Without going into any details into the matter, we can say that the importance of Carnot equation still remains unimpaired, because any *reversible* cycle whatsoever, without any restriction about the nature of the substance, about the operating conditions and sequences, and about anything, provided it is *completely reversible*, can be shown to be equivalent to a large number of Carnot cycles for each of which the Carnot equation is valid. Hence comes the importance of the Carnot equation.

The Concept of Entropy— If we transpose equation (2)-X for the second law suitably, we get

$$\frac{q_2}{T_2} + \frac{-q_1}{T_1} = 0$$

or $\dfrac{\text{Heat absorbed at } T_2}{T_2} + \dfrac{\text{Heat absorbed at } T_1}{T_1} = 0$ ... (3)-X

Since the equation derived for Carnot cycle is valid for any other reversible cycle and in fact since any *reversible* cycle can be shown to be equivalent in the limit to a large number of Carnot cycles, the above equation is valid for any *reversible* cycle whatsoever. Now, if we define a function S, such that

$$\triangle S = \frac{\text{Heat absorbed reversibly}}{\text{Temperature at which the heat is absorbed}} \qquad \text{... (4)-X}$$

or expressing as infinitesimal quantities

$$dS = \frac{dq_{rev}}{T}, \text{ or } S = \int \frac{dq_{rev}}{T} \qquad \text{...} \qquad \text{...} \qquad \text{... (5)-X}$$

we immediately see from the above general equation (3) that the sum of all $\triangle S$ terms over the whole cycle is zero. In other words, if we pass from a state A to a state B by any reversible path and again come back by any other reversible path to the original state A, the $\triangle S$ by the first path is equal to the $\triangle S$ by the second path or any other reversible path. Thus, S depends only on the state of the system and not in the least on how that state has been arrived at ; *i.e.*, S is a state function.

This property S defined by the above equation is called the entropy of the system.

Definition of Entropy—Hence, we define entropy as follows: The entropy difference between two states of a given system is equal to *the summation of all the q_{rev}/T-terms of all the steps necessary to bring about a reversible transformation between these two states, where* q_{rev} stands for the heat absorbed reversibly and T the corresponding temperature. This is mathematically expressed by equation (5) above.

It should be realised that this definition of entropy has nothing to do with the second law, but the latter's existence only makes the entropy, a state function. In other words, entropy has a definite value for each state of a system independent of the way in which that state has been attained and hence, the entropy change depends on the initial and final states, and not at all how the change of state has been brought about. Further, we cannot from the above equation measure the absolute entropy of a system, but we can always measure the change of entropy accompanying any transformation with the help of the above equation.

A very important point about entropy needs clarification at this stage. In the definition of entropy in the above equations it should be noted that the numerator is the amount of heat absorbed *reversibly*. Suppose we take in a vessel a gram atom of mercury and combine it with a gram atom of chlorine to form a gram mol of mercurous chloride at 25°C (298°K) and 1 atm. The system will liberate 31,300 calories of heat *i.e.* the system absorbs −31,300 calories. The entropy change $\triangle S$ of the system however will not be equal to −31,300/298 *e.u.* (entropy unit), because the above reaction has not been con-ducted reversibly. We can however conduct the same reaction reversibly in various ways, for example, in a reversible galvanic cell, by combining a calomel electrode with a chlorine electrode. If we now measure the heat absorbed by the galvanic cell where the same reaction is going on and divide this heat absorbed by the temperature (°K), we shall get the entropy increase in the above reaction. In fact, this electric cell will now evolve only 6,160 calories and so the entropy increase is only −6,160/298 = −20·5 e.u.

Entropy change during Isothermal Expansion of a Perfect Gas—It should be once again emphasised that the heat absorbed divided by the temperature is not equal to the increase in entropy but the latter is equal to the heat absorbed *reversibly* divided by the temperature. Suppose we take a gas and allow it to expand in a vacuum as in Joule's experiment. It is found that the gas does not absorb any heat *i.e.* $q=0$. But the entropy increase is certainly not zero because the above expansion has not been conducted reversibly. The entropy increase would be equal to the heat absorbed by the gas divided by the tempera-

ture if the gas was allowed to undergo the same expansion reversibly. In the above case we know (eqn. (1)), that when a perfect gas expands isothermally and reversibly from a volume V_1 to V_2 the heat absorbed is equal to the work done $= RT \ln V_2/V_1$ and therefore the entropy increase is this quantity divided by the temperature *i.e.* $R \ln V_2/V_1$. The student might wonder why though the system is absorbing no heat the entropy is still increasing. The reason is that we have proved above from the Carnot cycle that the entropy increase is independent of how the change is brought about and depends only on the initial and the final states of the system and is equal only to the heat absorbed *reversibly* divided by the temperature.

Comparative Study of the First and the Second Law— The *"modus operandi"* of the first law and that of the second law are basically similar. The first law introduces a new concept, a quantity called internal energy which is a characteristic of the state of the system; similarly, the second law introduces a new function, called entropy which is a characteristic of the state of the system and is not at all dependent on the path of a change. Also, in the first law we measure the change of internal energy by the energy we put into the system minus the energy we take out of it; similarly in the second law the entropy change is measured by the heat energy we put into the system divided by the corresponding temperature, summed up over the whole path of the change, *provided the whole change is conducted reversibly*. The concept of internal energy is as much a logical invention of the first law as is the concept of entropy of the second law. The only difference as we shall see later is that energy is indestructible and so easily appeals to our material comprehension whereas entropy always increases in any natural process, which is unlike any material change we are familiar with.

A Simpler Approach to the Concept of Entropy—There is another, though not strictly rigorous, way of looking into entropy which helps to clarify the fundamental idea behind it. The internal energy of any substance is composed of various contributions. A part might be the kinetic energy of the molecules, another part might be the vibrational energy of the molecules, another part might be due to intermolecular attraction, and other parts might be distributed in various other ways. Second law teaches us that all these various contributions of energy are not equally convertible into useful work. Without caring to consider which part of these different forms of internal energy is useful, the second law tells us that a portion of this energy is always unavailable and *entropy is a measure of this unavailable energy*. In fact we can regard *the entropy as the unavailable energy per unit temperature i.e.* entropy multiplied by the temperature (°K) gives the total quantity of energy which is unavailable for useful work.

The idea is very simple and can be illustrated with the help of our previous example of the reaction of calomel formation—

$$Hg + \tfrac{1}{2}Cl_2 = HgCl + 31,300 \ calories$$
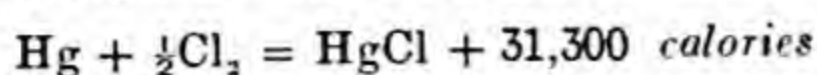
The heat of reaction of the above reaction at 25°C and 1 atm. is 31,300 calories. The question arises how much of it we can utilise for useful work? Is there any theoretical limit to the work which we can get out of this heat of reaction? The second law answers the question unequivocally. It first says that the
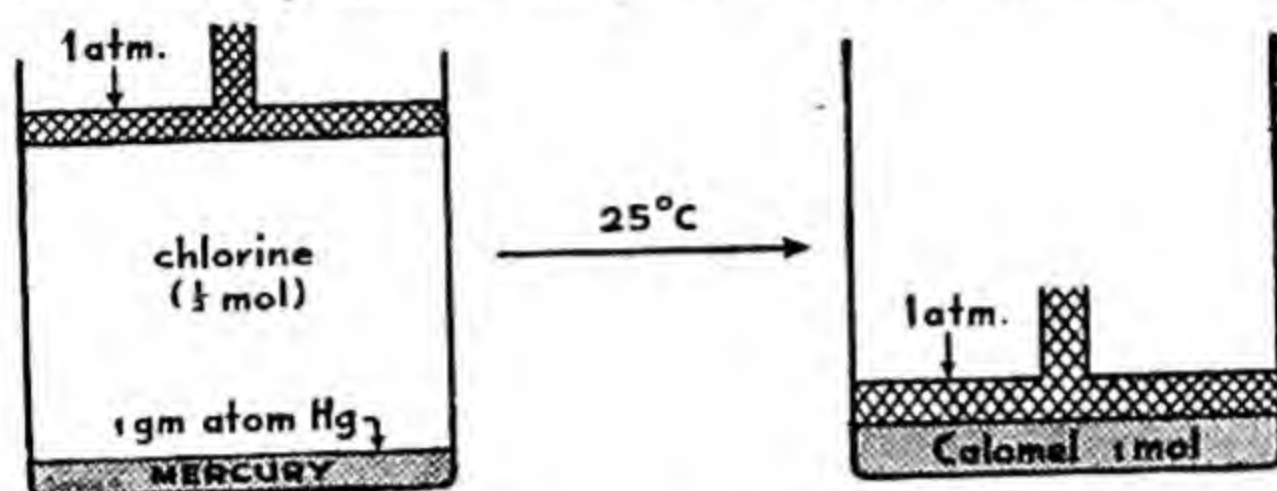

Fig. 46—Various energies in a chemical reaction.

Heat liberated in the above reaction,

$$Hg + \tfrac{1}{2}Cl_2 \longrightarrow HgCl; \ -\triangle H = 31,300 \ \text{calories}$$

Entropy change in the above process, $-\triangle S = 20{\cdot}6$ e. u.

∴ Unavailable energy = Entropy decrease $\times$ Temp $°K = 6{\cdot}160$ calories

∴ Available Energy for useful work, $-\triangle F = -\triangle H - (-T\triangle S)$.

$$= q_p - T(-\triangle S) = 31,300 - 6,160 = 25,140 \ \text{calories.}$$

whole can not be necessarily obtained as useful work. A part of it is to be lost which is proportional to the absolute temperature at which the reaction is carried out. And it also adds that this proportionality factor is the entropy change of this reaction and has a definite and measurable value under specified conditions. In other words, decrease of entropy multiplied by the absolute temperature gives the unavailable energy of the reaction.

In the above reaction the entropy decrease is 20·6 units. Therefore, the unavailable energy is entropy $\times$ temp $°K = 20{\cdot}6 \times 298 = 6,160$ calories. Hence second law tells us that out of the 31,300 calories evolved in the above reaction, 6,160 calories are unavailable, and however ingenious and perfect a machine we might construct we shall never get more than 25,140 calories of useful work out of this reaction.

Entropy as an Order-Disorder Phenomenon— There is a slightly different but very instructive way of looking at entropy. It is a common experience that there exists a natural tendency for an ordered set of things to get disordered by the interplay of natural forces. A platoon in formation if left to itself without control becomes a disordered crowd. A house i.e. an ordered assemblage of bricks, left to itself becomes a conglomerate of

bricks and so on. Since we know that the total entropy always increases in any natural process, we can therefore identify increase of entropy as increase of disorder. So, *entropy is a measure of the degree of disorder of a system.* This also fits in with our previous idea that an increase of entropy is equivalent to a loss of available work parallel with increase of disorder signifying less useful work. This is in analogy with our common social experience that a well-organised society is more efficient than an unorganised one. A quantitative expression for order-disorder is the probability of the thermodynamic state of a system *i.e.* the number of different arrangements of the constituent units which produce the system with the same properties. So, a system always tends to change by itself towards a state of maximum entropy *i.e.* maximum probability or maximum disorder or randomness of its molecules, and the more the disorder the less is the available work.

Free Energy Function—The concept of entropy as developed above is the most fundamental idea of thermodynamics. But, for convenience some other functions have been derived from it which have been found to be very useful for studies of chemical processes. Let us define a function A, called work content function (also called Helmholtz free energy) by the equation

$$A = E - TS \qquad \dots \qquad \dots \qquad \dots \quad (6)\text{-}X$$

$$\triangle A = \triangle E - T \triangle S \; (\textit{at constant temperature}) \dots \quad (7)\text{-}X$$

The student could immediately see from the definition of entropy we have given in the previous section that $T \triangle S$ is the unavailable energy and $\triangle E$ is the total energy and their difference $\triangle A$ is evidently the useful work. We however proceed to prove this.

According to the definition of entropy, we have at constant temperature

$$\triangle S = q_{rev} . T$$

and applying the first law to the same reversible process which, of course, at constant temperature yields the maximum work, we have

$$\triangle E = q_{rev} . - w_{max}$$

Substituting these two values in equation (7) we get

$$- \triangle A = w_{max} \qquad \dots \qquad \dots \qquad \dots \quad (8)\text{-}X$$

i.e. the decrease of the work content function A at constant temperature is equal to the maximum work done by the system.

We now define another function F, called free energy (also called Gibbs free energy, or Gibbs function) as defined by the following equations

$$F = H - TS \qquad \dots \qquad \dots \qquad \dots \quad (9)\text{-}X$$

$$\triangle F = \triangle H - T \triangle S \; (\textit{at constant temperature}) \quad \dots \quad (10)\text{-}X$$

Evidently, since $H = E + PV$, and $F = A + PV$, the free energy function F, bears the same relation to the work content function A, as the heat content (enthalpy) H does to the internal energy, E.

Suppose a reversible change takes place at constant temperature, T and at constant pressure, P and the system changes in volume by $\triangle V$. The work of expansion of the system is $P \triangle V$ and suppose the system does an additional amount of work* w_1 which latter we shall call net work. Hence, the total work done by the system $w = w_1 + P \triangle V$. Hence we have from the first law,

$$\triangle E = (q_{rev.})_p - w = (q_{rev.})_p - w_1 - P \triangle V$$

$$\triangle E + P \triangle V = (q_{rev.})_p - w_1$$

By equation (6), $\triangle H = (q_{rev.})_p - w_1$

From second law eqn., $\triangle S = (q_{rev.})_p / T.$

Substituting these values in the definition of free energy function (eqn. 10), we have

$$\triangle F = (q_{rev.})_p - w_1 - T (q_{rev.})_p / T$$

$$= - w_1$$

$$- \triangle F = w_1 = w - P \triangle V \qquad \qquad \ldots \qquad \ldots \text{(11)-X}$$

Hence, *the decrease in free energy at constant temperature and at constant pressure is equal to the net work i.e.* the total work minus the pressure-volume work due to the system's own volume change.

The students should be careful to avoid the fallacy that any reversible process yields the maximum work. This is quite erroneous and misleading. The main idea is that any reversible process yields more work than if the same process is conducted irreversibly. But the same process can be brought about in an infinite number of reversible ways and the yield of work may be different in each case. In other words, given only the initial and the final conditions, it is not possible to state the maximum amount of reversible work obtainable out of the change. Only if we put another additional restriction that the temperature is constant throughout, the maximum reversible work, w becomes definite and fixed, and equals the decrease in the work content function i.e. $(- \triangle A)$ of the system.

The student should now carefully note the imposed conditions of equations (5) and (11) i.e. $- \triangle A = $ total work, provided temperature is constant and $- \triangle F = $ net work provided both temperature and pressure are constant. Also note that the temperature is to be maintained constant throughout the change because we have used the equation $T \triangle S = q_{rev}.$

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* This point should not introduce any difficulty. In any reversible change, the total work obtainable is not only the pressure $\times$ volume work due to expansion or contraction of the system but also there are additional amounts of work. As for example in the calomel formation reaction as discussed above the pressure — volume work of the system is only $-\frac{1}{2}RT$ (about-300 calories) but the available useful work is a few thousand calories.

which is otherwise not valid, but the only restriction about pressure is in the term $P\triangle V$ which only imposes that the initial and the final pressures are to be the same but allows us complete liberty to change the pressure if we want during the transformation provided we adhere to the overall restriction that the process is reversibly conducted. This is a very important point and should be carefully noted to avoid later confusion.

Total Entropy Change in Reversible and Irreversible Processes —So far we have been considering the entropy change of the system only. For example, in an isothermal reversible expansion of a gas we calculated in a previous section the increase in entropy of the gas, but during the above process not only the gas but also the surroundings have also undergone a change in entropy. Since the process is ideal, the surroundings have lost an exactly equal amount of heat at the same temperature as the gas has gained during its reversible expansion. Since entropy increase is defined as heat absorbed reversibly divided by the temperature we immediately see that the increase of entropy of the gas is equal to the decrease of entropy of the surroundings. That is, the total entropy change in the above reversible process is zero. This is however true of any reversible process as is implied in the definition of reversibility and entropy. Hence we can write that for any reversible process,

$$\triangle S = \triangle S_1 + \triangle S_2 + \triangle S_3 + ... = 0 \qquad ... (12)\text{-}X$$

where $\triangle S_1$, $\triangle S_2$, $\triangle S_3$, etc., represent the entropy increase of all portions of matter which have suffered any change of entropy. In other words if we had an isolated system *where all changes take place reversibly* the total entropy like energy would remain constant.

Consider now the same change conducted irreversibly. Taking the extreme case, suppose the gas does the same expansion against a vacuum. In this case no heat will be absorbed from the surroundings and so the surroundings will not undergo any change in entropy. However, the gas has undergone a change of entropy exactly equal to what it did in the previous reversible expansion, because the entropy increase does not depend on the actual amount of heat absorbed by the gas but depends only on the heat which *the process would have absorbed if it was conducted reversibly*. Hence, after the above irreversible expansion the total entropy will be higher than that at the beginning. The same holds true as long as the expansion is irreversible, because in all such cases the loss in heat by the environment will be less than what it would have lost in a reversible process. This condition applies to all irreversible processes whatsoever and so we come to a very important conclusion that *in any irreversible process the total entropy increases i.e.*

$$\triangle S = \triangle S_1 + \triangle S_2 + \triangle S_3......> 0 \qquad ... \qquad ... (13)\text{-}X$$

This fact led Clausius to tersely summarize the first and the second laws by saying that *the energy of the universe remains*

*constant, and the entropy of the universe tends towards a
maximum.*

The significance of the above equation (13) is a little discon-
certing from our material viewpoint. Since increase of entropy
means increase of unavailable energy (*vide* P. 134), the above
equation signifies that whatever happens round us makes some
energy unavailable though the total energy remains constant.
Consider by a rough calculation of entropy, what happens when
a hot body equalises its temperature with a cold body. The hot
body has lost q calories and the cold body has gained q calories.
But since the average temperature T_2 of the hot body is higher
than the temp. T_1 of the cold body, the entropy decrease of the
hot body (q/T_2) is less than the entropy increase of the cold
body (q/T_1) and hence the total entropy increases in this process.
This is true for all natural *i.e.* spontaneous processes. Hence we
can write

$$\sum dS = \sum \frac{dq\,rev.}{T} = 0 \text{ for a reversible process}$$
$$\sum dS = \sum \frac{dq\,rev.}{T} > 0 \text{ for any natural process} \qquad \Bigg\} \quad \dots \text{ (14)-X}$$

Since the entropy increases in any natural *i.e.* spontaneous
process, it is evident that the universe is slowly but surely drifting
towards the state of maximum entropy. And, once that state is
attained, all production of useful work would cease and so life as
we understand would come to a complete end. This inevitable and
irrevocable transition towards an ultimatum was fully realised by
Clausius in the last century when he made the grim prophecy of
the ultimate 'thermal death' of the universe when no work would
be possible owing to an absolute equalisation of temperature.

Conditions of Equilibrium —The above equations supply us
a clue to the most general statement of the conditions of
equilibrium. Since all stages of a reversible process are really
equilibrium conditions, any system which is in equilibrium must
satisfy the condition,

$$dS = 0 \qquad \dots \qquad \dots \qquad \dots \text{ (15)-X}$$

If we leave hydrogen with chlorine, they go on changing
continuously to form HCl because by so doing the total entropy
is increasing. A hot body gives heat to a cold body because
the total entropy increases by this process. It should be care-
fully noted that when hydrogen and chlorine combine to form
HCl, the entropy of the system does not increase, in fact, it
decreases. But the above equation (14) says that the total entropy
increases *i.e.* in this case the increase of entropy of the surround-
ings must be greater than the decrease of entropy of the hydrogen-
chlorine mixture. When the equilibrium is reached the entropy
does not change any more.

Though the above condition (equation 15) is a perfectly general statement of the condition of equilibrium, for our chemical purpose we can narrow it down under some definite conditions to some easily measurable property of the system itself independent of the change in the surrounding. Suppose we conduct a chemical reaction between hydrogen and oxygen *at constant temperature and pressure* to form water vapour. The system changes because there is a driving force behind it which if properly harnessed will yield work. This work is something which is in addition to the pressure-volume work owing to the change of volume of the system and is called the net work of the system. Hence, only a reaction which can furnish some net work can proceed naturally and when it has lost this potentiality, no further change in the system will take place. Since net work is the negative of the change in free energy we can immediately write,

$$\Delta F = \text{negative......} for\ a\ natural\ process$$
$$\Delta F = \text{positive......} for\ an\ unnatural\ process \qquad (16)\text{-X}$$
$$\Delta F = 0 \qquad for\ an\ equilibrium$$

We draw the attention of the students again to the sign of ΔF with relation to the net work produced. The function F is a measure of the net work content *i.e.* free energy content of the system and hence, any decrease of F(*i.e.* $\Delta F = F_2 - F_1 = $ negative) means that the system has produced net work. This function has been thus defined because we want to concentrate our attention on the system itself.

Chemical Affinity and Free Energy —The free energy of a chemical reaction is the driving force or the affinity behind the reaction and only processes for which ΔF is negative may take place spontaneously. For the reaction.

$$H_2 + \tfrac{1}{2}O_2 = H_2O : \Delta F_{298}{}^{\circ}{}_K = -56,690 \text{ calories}$$
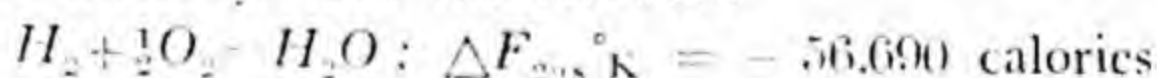
means that if we convert hydrogen and oxygen to a mol of water at unit pressure and 25°C. the system decreases in free energy by 56,690 calories. In other words if we had conducted the same reaction reversibly, we could get 56,690 calories of work, and hence it is a spontaneous reaction.

Another application of this concept is illustrated by the following two equations which show two possible ways of decomposition of hydrogen peroxide and the corresponding theoretically calculated free energy changes.

(a) $H_2O_2 = H_2O + \tfrac{1}{2}O_2 : \Delta F = -25,090$ cals
(b) $H_2O_2 = H_2 + O_2 : \qquad \Delta F = -31,470$ cals
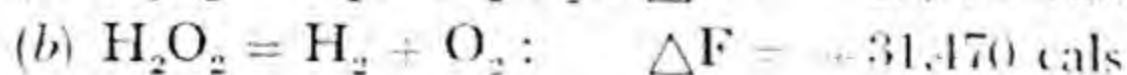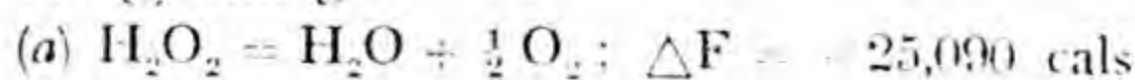
It is thus seen why hydrogen peroxide is more prone to decompose to water and oxygen rather than to hydrogen and oxygen.

A negative value of ΔF does not necessarily mean that the process does take place spontaneously. It merely shows the possibility of the reaction provided the conditions are right.

Thus a mixture of hydrogen and oxygen can remain indefinitely without any detectable change. When a catalyst like platinised asbestos is introduced, the two react with explosive violence. The reaction would not have occurred even with catalysts if the thermodynamic possibility as shown by a decrease of $\triangle F$ owing to the reaction was not present. Suppose we want to manufacture ammonium nitrite by a new reaction,

$$N_2 + 2H_2O = NH_4NO_2$$
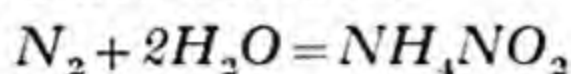
Instead of searching for catalysts and running innumerable trial experiments to know the possibility of such a scheme, the question might be settled by a simple calculation of $\triangle F$ from the existing thermal data and see whether it is a negative or a positive quantity. Actually it is found that $\triangle F$ is a large positive quantity for the above reaction and hence we predict that the reaction has little chance of being a commercial success.

For determination of the free energy of a chemical reaction, which is undoubtedly one of the most important applications of thermodynamics to chemistry, the student is referred to Ch. XIV.

Variation of Maximum Work with Temperature : Gibbs-Helmholtz Equation—The second law equation as derived from Carnot cycle gives the maximum work obtainable from a given quantity of heat whereas the first law relates this heat to the internal energy. Hence, if we eliminate the quantity of heat, q between these two equations, we get a simple relationship between the internal energy and the maximum work. Thus, from Carnot cycle,

$$w_{max} = q_2 \frac{T_2 - T_1}{T_2}$$

If $T_2 - T_1$ is very small the work obtained will also be very small and expressing both of them by infinitesimals, we have

$$dw_{max.} = q \cdot \frac{dT}{T} \text{ or, } q = T \cdot \frac{dw_{max}}{dT}$$

Substituting the value of q in the first law equation,

$$\triangle E = q - w, \text{ we get, } \triangle E + w_{max} = T \frac{dw_{max.}}{dT} \quad \dots \quad \dots \quad (17)\text{-X}$$

which as well as its another form, viz., equation (18) is known as the Gibbs-Helmholtz equation.

The significance of this equation is more easily appreciated if it is written in the form where $-\triangle F$ is substituted for w, i.e.

$$w_{max} - (-\triangle E) = T \frac{dw_{max.}}{dT} \text{ or, } \triangle F - \triangle H = T \frac{\partial \triangle F}{\partial T} \quad \dots \quad (18)\text{-X}$$

which means that the maximum work done by a process is not generally equal to the decrease in internal energy, but the two are unequal by an amount shown by the right hand side of the Gibbs-Helmholtz equation.

Gibbs-Helmholtz equation is undoubtedly one of the most useful equations of thermodynamics as it embodies the essence of both the first and the second law, and almost any relation of thermodynamics can be deduced from it or its various modifications. We give below an illustration.

Variation of Vapour Pressure with Temperature : Clapeyron Equation—The Gibbs-Helmholtz equation can be applied to any isothermal process or change if we can conduct it reversibly. Suppose we want to apply it to the process of evaporation. If we take a mol of a liquid and want to convert it reversibly into vapour, we can easily do it by confining it in a vessel under a weightless frictionless piston and applying a pressure just lower than its saturation pressure. The piston will be pushed up reversibly until the mol of water has been completely evaporated. In this change since the pressure is constant throughout, the system will do an amount of work given by the pressure multiplied by the change of volume. If the molar volume of the vapour is V_2, and that of the liquid is V_1, and the saturation pressure is P, we have work done=pressure x volume increase, i.e.

$$w = P(V_2 - V_1)$$

Differentiating with respect to temperature at constant change of volume, $(V_2 - V_1)$

$$\frac{dw}{dT} = (V_2 - V_1)\frac{dP}{dT}$$

The system will also be absorbing heat from the surroundings equal to its latent heat of evaporation. Let the latent heat be L which substituted for q in the first law equation gives

$$\triangle E = L - w$$

Substituting these three equations in the Gibbs-Helmholtz equation (17) we get

$$(L - w) + w = T(V_2 - V_1)\frac{dP}{dT}$$

$$\text{or} \quad \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \quad \dots \quad \dots \quad (19)\text{-}X$$

which is Clapeyron equation.

Since the heat absorbed at constant temperature and pressure is equal to $\triangle H$, we can substitute $\triangle H$ for L, to get the more familiar form of Clapeyron equation,

$$\frac{dP}{dT} = \frac{\triangle H}{T(V_2 - V_1)} \quad \quad \dots \quad \dots \quad (20)\text{-}X$$

This equation gives the rate of variation of equilibrium pressure with temperature during any phase change and so is applicable not only to vaporisation but to any change of state say, the conversion of a solid into a liquid, or one allotropic form into another, where $\triangle H$ is the heat absorbed by one mol during the

transition and V_2 and V_1 are the molar volumes of the second phase and the first phase respectively.

Change of F.P., B.P., and Transition Temperature with Pressure—Equation (20) which gives the variation of the equilibrium pressure with temperature can also be used to calculate the change of transition temperature (including melting point, boiling point, etc.) with pressure, because the latter is merely the reciprocal of equation (20). This may be illustrated by calculating the change of M.P. of ice with pressure.

Density of ice, $0°C = 0.9168$ g/cc $\therefore V_1 = 18/0.9168$ $c.c./mol.$

Density of water, $0°C = 0.9998$ g/cc $\therefore V_2 = 18/0.9998$ $c.c./mol.$

Latent heat of fusion $= 80$ cal/gm $\therefore L = 18 \times 80$ $cal/mol.$

$$\therefore \frac{dT}{dP} = \frac{T(V_2 - V_1)}{L}$$

$$= \frac{273 \times 18 \ (1/0.9998 - 1/0.9168)}{18 \times 80}$$

$$= -3.09 \ degree - cc/cal$$

Now, 1 atmos $= 76 \times 13.6 \times 981$ $dyne/cm^2$ $(= dyne \cdot cm/cc = erg/cc)$

$= 76 \times 13.6 \times 981/4.2 \times 10^7$ cal/cc

Hence, 1 $cc/cal = 0.0241$ $atmos^{-1}$

$$\therefore \frac{dT}{dP} = -3.09 \times 0.0241 = 0.0745 \ degree \ atmos^{-1}$$

So, the melting point of ice at $0°C$ is lowered by $0.074°C$ by 1 atm. increase of pressure. Note carefully the method by which units have been handled and it is urged that this method should always be followed when complicated units arise.

The student should carefully note that $V_2 - V_1$ is negative for the transition ice $\longrightarrow$ water, and so the melting point of ice is *lowered* by increase of pressure. For the transformation water $\longrightarrow$ steam, $V_2 - V_1$ is positive and so boiling point is *raised* by increase of pressure. Further the volume change during evaporation is a few order higher than the corresponding change during melting, and so though the melting point of ice is lowered by less than a tenth of a degree if the pressure is increased to two atmosphere, the boiling point increases by about $20°C$ by the same pressure change.

Clausius-Clapeyron Equation—The Clapeyron equation admits of some useful simplification if applied to the vaporisation of a liquid. Since the volume of a liquid is very small compared to its own vapour, we can neglect V_1 in comparison with V_2, when equation (20) becomes

$$\frac{dP}{dT} = \frac{\triangle H}{TV_2}$$

Also, since V_2 is the volume of a gas we can apply the ideal gas equation $PV = RT$ which makes V_2 equal to RT/P, which substituted in the above equation gives

$$\frac{1}{P}\frac{dP}{dT} = \frac{\triangle H}{RT^2}$$

$$\frac{d \ln P}{dT} = \frac{\triangle H}{RT^2} \qquad \dots \qquad \dots \quad (21)\text{-X}$$

which is called the Clausius-Clapeyron equation.

This equation is only approximate since we have used two approximations in its derivation; we have neglected V_1 and we have used the perfect gas equation. The latter approximation usually affects the results more than the former.

The above equation (21) can be integrated by assuming $\triangle H$ independent of temperature as follows.

$$d \ln P = \triangle H \; dT/RT^2$$

$$\int d \ln P = \frac{\triangle H}{R} \int \frac{dT}{T^2}$$

$$\ln P = - \frac{\triangle H}{RT} + \text{constant} \qquad \dots \quad (22)\text{-X}$$

i.e. if the logarithm of the vapour pressure of a liquid is plotted against the reciprocal of the absolute temperature, a straight line is obtained having a slope equal to $-\triangle H/2\cdot303R$.
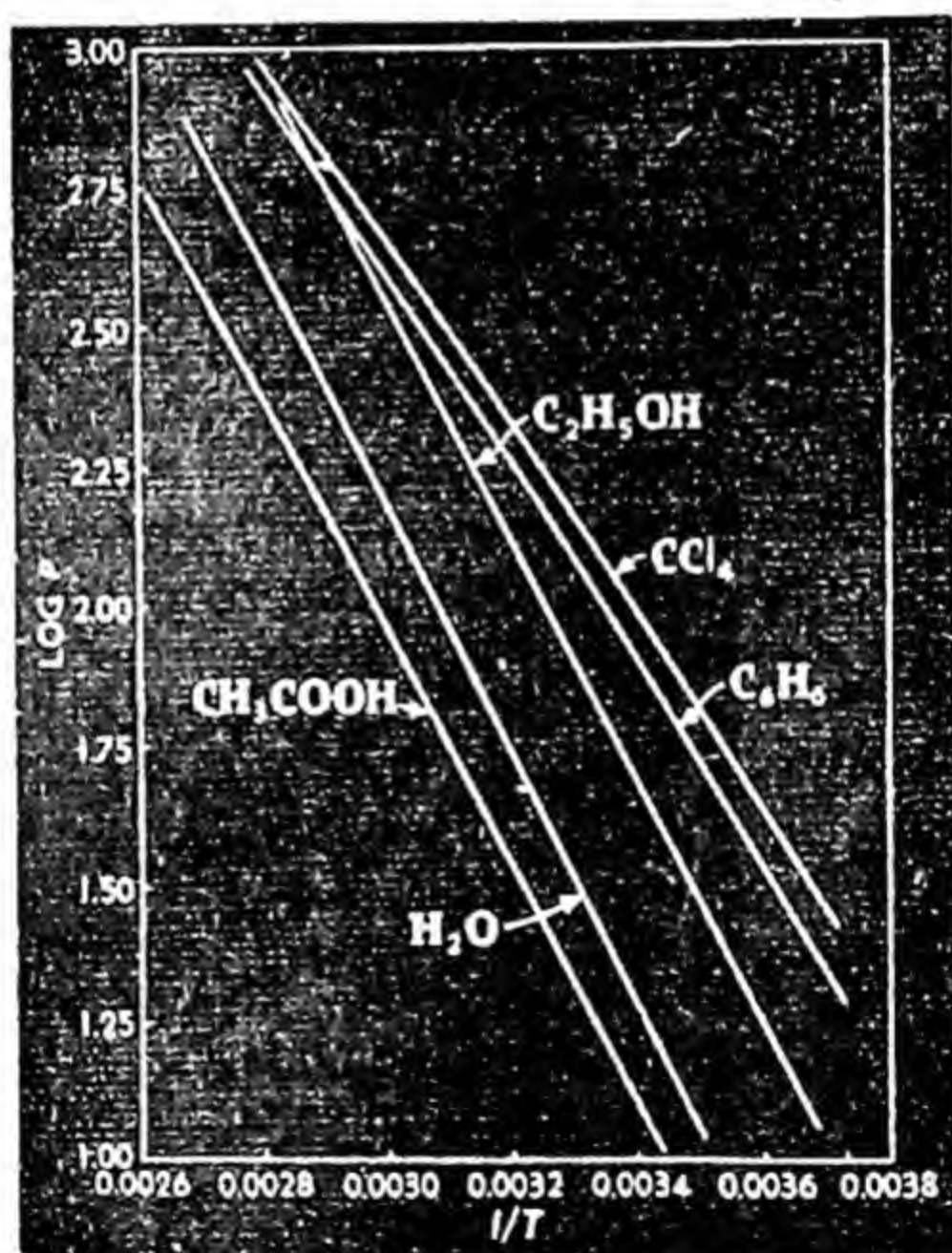

Fig. 47—Vapour Pressure of Liquids on Logarithmic Scale

This is illustrated in Fig. 47 where log P has been plotted against $1/T$ for a few common liquids. It will be observed that the experimental data fall very closely on straight lines.

If we had integrated between limits say T_1 and T_2 we would have obtained

$$\log P_2 - \log P_1 = \frac{\Delta H}{2 \cdot 3 R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ldots \text{(23)-X}$$

From this equation knowing the vapour pressures at two temperatures we can calculate the latent heat of evaporation of a liquid, or alternatively, knowing the latent heat of evaporation and the pressure at any temperature we can calculate the vapour pressure at any other temperature.

EXERCISE

(1) Distinguish between reversible and irreversible changes giving examples.

(2) Discuss the reversibility or otherwise of the following changes :—

(a) Explosion of a mixture of H_2 and O_2.

(b) Conversion of a mol of water to steam at 100° and 760 mm.

(c) Heating a liquid at constant volume from T_1 to T_2.

(d) Charging and discharging of a lead accumulator.

(e) $Cu^{++} + Zn = Zn^{++} + Cu$, (i) conducted in a beaker and (ii) in a Daniel cell.

(3) One mol of an ideal gas held at 10 atm. in a cylinder is reduced to one atmosphere in two stages, viz. first to 5 atmosphere and then to 1 atmosphere, temperature being 27°C throughout. Calculate the total work done in these two steps and compare it with the total work obtainable from the same overall change, if carried out reversibly and isothermally.

[31·98 ; 56·64 litre-atm.]

(4) What is the maximum work obtainable in a reversible and isothermal expansion of a mol of ethylene from 1 litre to 100 litres at 27°C, assuming that the gas follows van der Waals equation? Use a and b values given in Ch. III. What would be the value for a perfect gas?

[110·3 lit-atm. ; 113·3 lit-atm.]

(5) Calculate the maximum work obtainable in the reversible and isothermal expansion from P_1 to P_2 of a gas following the equation $PV^2 = RT$. In what essential way does the result differ from the perfect gas value?

(6) Deduce an expression for the efficiency of a reversible engine, and from the expression develop the concept of entropy and show that the latter is a state function.

(7) Discuss the statement with its full implication, "Entropy of the universe tends towards a maximum".

(8) Deduce an expression for the difference between the reversible heat and the irreversible heat of any change as a function of temperature.

(9) Deduce Clapeyron equation for the phenomenon of melting. Why does the M.P. of water decrease whereas that of pure paraffin wax increase with pressure?

(10) How do you obtain the heat of vaporisation of a liquid from change of vapour pressure over a temperature range?

(11) Calculate q, w and $\triangle E$ when a mol of a perfect gas at N.T.P. is reversibly compressed (i) isothermally and (ii) adiabatically to 2 atmospheres. (Assume $C_v = \frac{3}{2} R$).

[$q = w = -378$ cals ; $\triangle E = 0$; $q = 0$, $\triangle E = -w = 262$ cals]

(12) Why is the change of boiling point with pressure is nearly the same for all liquids but the change of freezing point widely different.

(13) Entropy has the same unit as the universal gas constant. Discuss the truth or otherwise of the above statement.

10

CHAPTER XI

SOLUTIONS: GENERAL

Definition—A mixture of two substances may be homogeneous, or heterogeneous, the former being defined as one, in which very close observation cannot reveal the existence of any surface of separation between two dissimilar substances and the composition is uniform all throughout. Such a homogeneous mixture is called a true solution. So, we can formally define *a solution as a perfectly homogeneous mixture of two or more substances whose composition may be varied between certain definite limits.*

There is a class of solutions, which appears homogeneous to the naked eye but is really heterogeneous as can be seen under a microscope or ultra-microscope. Such a solution is not a true solution but is called a colloidal solution. Milk is an example to the point for, though it appears perfectly homogeneous to the naked eye, under the microscope it is seen to consist of fine droplets of fat suspended in a liquid medium.

Different Types of Solutions —Substances in different physical states may form solutions and the following types of solutions are easily realised.

1. *Solution of Gases in Gases.* Example: any mixture of gases as for example, air, electrolytic gas $(2H_2+O_2)$, etc.

2. *Solution of Gases in Liquids.* Example: carbonated drink or mineral water consisting of CO_2 gas (and other solutes) dissolved in water.

3. *Solution of Gases in Solids.* Example: absorption of H_2 by palladium.

4. *Solution of Liquids in Liquids.* Example: a mixture of alcohol and water.

5. *Solution of Liquids in Solids.* Example: liquid metallic mercury is dissolved by some metals such as gold.

6. *Solution of Solids in Liquids.* Example: sugar in water or the usual types of solutions.

7. *Solution of Solids in Solids.* Example: alloys, for example, brass is a solid-solid solution of zinc and copper.

Examples of true solutions of liquids in gases or solids in gases are not realisable experimentally. Smoke, mist etc., cannot be regarded as examples of true solutions of these types for, they are really heterogeneous systems. The student may be led to think that when camphor disappears in air it is certainly a solution of solid camphor in air, but it is merely a case of a solution of one gas in another.

Solvent and Solute —Usually we have to deal with solutions in which one of the members is present in a large excess over the other; the substance which is present in lesser amount is called

the *solute* and the other component present in excess is called the *solvent*. It should be clearly recognised that this distinction of solute and solvent is quite arbitrary and cases *e.g.* completely miscible pair of liquids or gases, may arise where one is quite justified to fix up either of the components as the solvent or the solute.

Modes of Expressing the Composition of a Solution—For physico-chemical purposes, it is customary to express the composition of a solution in either of the following three ways— (a) *molarity*, (b) *molality* and (c) *mol-fraction* of which method (a) is widely used.

(a) **Molarity and Normality** —*The number of gram molecules of solute dissolved in 1000 c.c. of the solution is called the molarity of the solution.* If a gms of solute of molecular weight M is dissolved in a total volume of V litres the molarity 'c' of the solution will be, (since, number of moles = a/M),

$$c = \frac{a}{M} \times \frac{1}{V} \qquad \ldots \qquad \ldots \qquad \ldots \quad (1a)\text{-XI}$$

∴ *molar concentration × molecular weight = gms per litre.*

Exactly similar relations are valid with normality and equivalent weight.

∴ *normality × equivalent weight = gms per litre.*

The advantages of this method of expressing concentration are twofold; firstly, almost all the fundamental equations of physical chemistry, such as the equation of van't Hoff, the equation for the law of mass action, etc., are valid if all the concentration terms are expressed in molarity, and secondly, it simplifies calculation for, if a solution is, say, 0·5 normal with respect to sodium chloride, without further calculation we may also put it to be 0·5 normal with respect to sodium and chlorine separately.

(b) **Molality or Weight-Molar Concentration**—This method of expressing concentration is extensively used by modern chemists. *The molality of a solution is expressed by the number of gram molecules of solute dissolved per 1000 gms of solvent.* This method has the advantage that concentrations are expressed on the basis of weight and so, the strength of a given solution is independent of temperature and standard solutions can be easily prepared with the help of a balance. Standard solutions prepared on this basis are called *weight-molar* solutions. If 'a' gms of solute of molecular weight M (*i.e.* a/M gm molecules) are dissolved in 'b' gms. of solvent, the molality of the solutions is

$$C_m = \frac{a \times 1000}{M \times b} \qquad \ldots \qquad \ldots \qquad \ldots \quad (1b)\text{-XI}$$

If the specific gravity of a solution is known, the conversion from

molarity to molality or *vice versa* can be easily done (*Vide example* 1).

(c) **Mol-fraction**—The idea of expressing concentration in mol fraction is applicable to a solution consisting of any number of components. Take for example the simple case of two components A and B. If in a solution containing A and B only, the number of moles of A present be N_a and the number of moles of B present be N_b, the total number of moles present will be $N_a + N_b$. Then, mol-fraction of $A = \dfrac{N_a}{N_a + N_b}$ and mol-fraction

of $B = \dfrac{N_b}{N_a + N_b}$; and therefore, the *mol fraction of a substance is defined as the ratio of the number of moles of that substance present to the total number of moles in solution.* Therefore, concentration of a given solution varies slightly with temperature if the concentration is expressed in molarity or normality but is independent of temperature if expressed in mol fraction or molality.

Mol-fraction multiplied by 100 is called mol per cent. The physical significance of mol per cent is the total number of molecules of any component present per 100 molecules of the mixture. The calculation of concentration in different units is made clear by the following example.

EXAMPLE 1. *A solution of sodium chloride is prepared by dissolving 10 gms of the salt and adding just sufficient water to make the total volume 100 c.c. Express the concentration in* molarity, molality *and* mol-fraction. (*Density of the solution*—1·95).

(i) 100 c.c. soln. contains 10 gms = 10 ÷ 58·5 = 0·1709 mols.

∴ 1 litre contains 1·709 mols.

∴ Molar concentration = no. of mols, per litre = *1·709 mol*/litre.

Since equivalent wt. of NaCl is equal to its mol. wt. (= 58·5) the strength of solution in normality = 1·709 gm equivalent per litre.

(ii) 100 c.c. of the solution weighs 100 × 1·05 = 105 gms. of which 10 gms. (= 0·17 mols) are due to the solute and so, 95 gms. are due to the solvent.

∴ Molal concentration = number of mole per 1000 gms. of solvent

$$= \frac{0·1709}{95} \times 1000 = 1·799 \text{ mols per 1000 gms. of water.}$$

(iii) 100 gms water = 100 ÷ 18 = 5·55 mols,

10 gms of NaCl = 10 ÷ 58·5 = 0·1709 mols.

∴ Total number of mols = 5·55 + 0·1709 = 5·7209

∴ Mol-fraction of NaCl = $\dfrac{·1709}{5·72}$ = 0·02987.

Mol-fraction of water = $\dfrac{5·55}{5·72}$ = 0·9701.

Hence, mol per cent of common salt is 2·97 and that of water is **97·01**.

A. SOLUTION OF GASES IN GASES

Dalton's Law of Partial pressure —Gases are completely miscible with one another in all proportions, and so can form solutions (*i.e.* mixtures) with one another in any proportion. Usually their concentrations in a mixture are expressed by their respective partial pressures. The *partial pressure* of any component of a mixture of gases is defined as the pressure that this component would exert, had it been alone present in the total volume occupied by the mixture. A simple rule was put forward by Dalton in 1802 to express the pressure relationships of a gaseous mixture. This rule, which is known as *Dalton's law of partial pressure* states that *"the pressure exerted by a gaseous mixture is equal to the sum of the pressures which the constituents would exert if each occupied separately the volume of the mixture"* or, in other words, *the total pressure in a mixture of gases is equal to the sum of their partial pressures.*

Like the gas laws, Dalton's law holds good accurately only at very low pressures. Deviations occur at higher pressures due to the same reasons as cause ordinary gases to depart from ideal gas laws. Up to a pressure of a few atmospheres this law is generally assumed to be approximately true and is extensively used in engineering calculations.

The interpretation of Dalton's law of partial pressure from the standpoint of kinetic theory is very simple. Since a gas contains much void space, the introduction of a second gas in the same space offers no difficulty of accommodation and merely increases the number of molecules per c.c. and hence, the pressure. This is illustrated diagrammatically in Fig. 48, wherein we have attempted to convey the idea that the mixture, A and B is a superposition of A and B on a molecular scale.
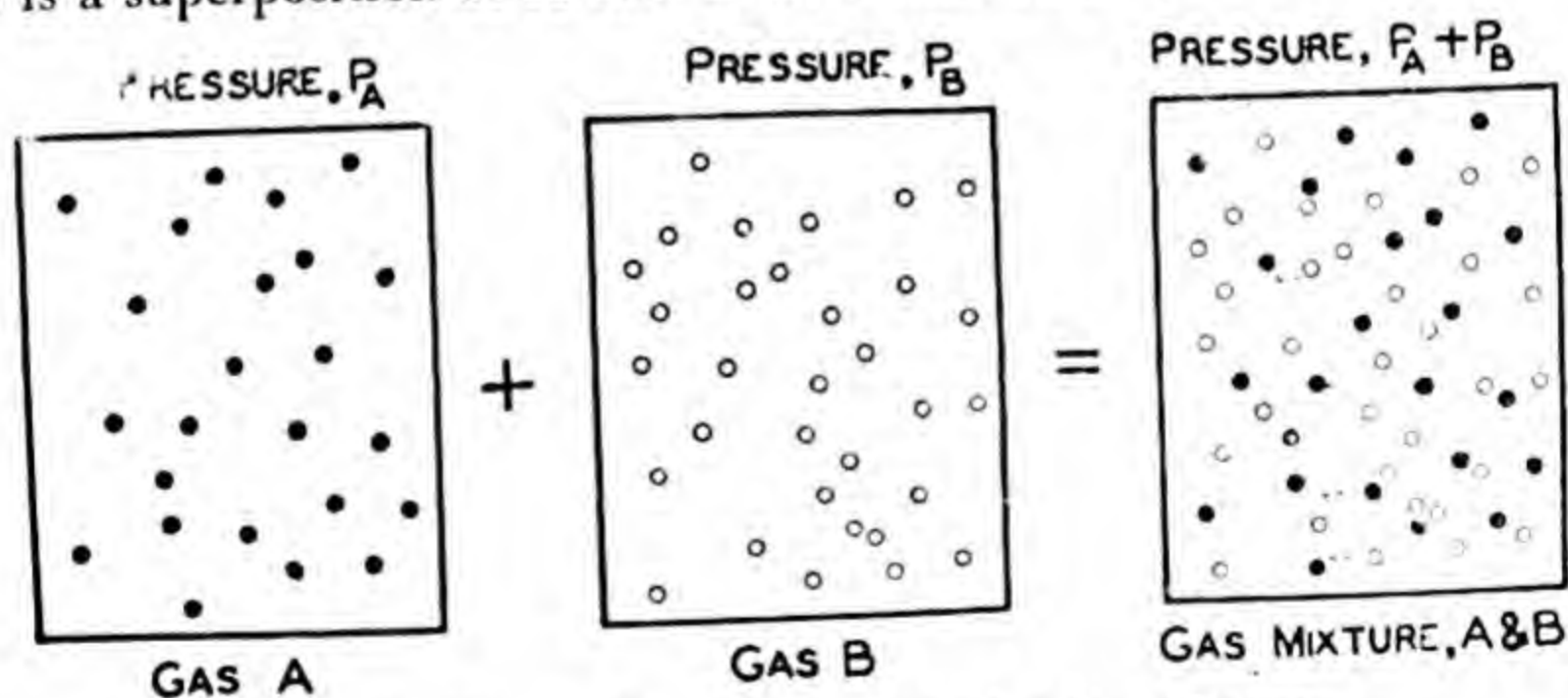

Fig. 48—Kinetic Theory Picture of a Gas Mixture.

EXAMPLE 2. *Calculate the total pressure in a mixture of say, 4 gms of oxygen and 2 gms of hydrogen confined in a total volume of one litre at 0°C.*

First of all, we have to regard that oxygen alone is present in the total volume of 1 litre and calculate its pressure which is its partial pres-

sure in the mixture. Similarly, we have to calculate the partial pressure of hydrogen. The total pressure will be the sum of these two partial pressures. If P_1 is the partial pressure of oxygen, then according to the equation $P_1V = (g/M)RT$, we have $P_1 \times 1$ litre $= 4/32 \times 0.0821 \times 273$, so $P_1 = 2.8$ atm.

Similarly $P_2 \times 1$ litre $= 2/2 \times 0.0821 \times 273$, so $P_2 = 22.4$ atm.

$\therefore$ the total pressure $P = P_1 + P_2 = 25.2$ atmospheres.

Note that, weight for weight, the lighter gas has a higher partial press.

Calculation of Partial Pressure—This law is of great importance in view of the fact that it is not the total pressure of the gas mixture but the partial pressures of the components which determine the physico-chemical equilibria. For example, the partial pressure of oxygen in the inhaled air determines the extent to which hemoglobin is converted to oxyhemoglobin. Combined with perfect gas equation, Dalton's law gives a very simple relation for partial pressure calculations.

If in a volume V, there are n_1 mols of A, n_2 mols of B, n_3 mols of C and so on, and the corresponding partial pressures are p_1, p_2, p_3, etc., respectively, then according to Dalton's law,

$$P = p_1 + p_2 + \dots \quad \dots \quad \dots \quad \dots \quad (i)$$

where $p_1 = n_1 RT/V$; $p_2 = n_2 RT/V$; etc.   ...   ... (ii)

since each component conforms to the gas equation independent of the other.

Or, $P = (n_1 + n_2 + \dots) RT/V = NRT/V \quad \dots \quad \dots \quad (iii)$

where N is the total number of mols present in the mixture. Combining (ii) and (iii) we get

$$p_1 = \frac{n_1}{N} P ; \quad p_2 = \frac{n_2}{N} P ; \dots \quad \dots \quad \dots \quad (2)\text{-}X$$

i.e. the partial pressure of any component in a gas mixture is equal to the product of its mol fraction and the total pressure.

Methods of expressing Gas Composition—Instead of partial pressure method or the other methods discussed in the previous section the composition of a gas is often expressed by **percentage by volume** of each component. The latter is defined as the volume per cent which each species would occupy if it is subjected to the total pressure of the mixture. It can be easily proved that *the volume per cent of any species in a gas mixture is equal to its mol per cent* and hence percentage by volume has the additional significance that it gives the mol per cent of the species directly. The proof is given below for 100 litres.

$P = P_1 + P_2 + P_3 + \dots = (n_1 + n_2 + \dots) RT/100 ;$

since by definition, $P_1 \times 100 = n_1 RT ; P_2 \times 100 = n_2 RT ; \dots \dots$

Let the volume percentage of the first gas be r_1 ; then by definition of volume per cent, we get,—

$P r_1 = n_1 RT$, or $r_1 = \frac{n_1}{P} RT = \frac{n_1}{n_1 + n_2 + \dots} \times 100 = $ mol fraction $\times 100$

$= $ mol. per cent of A

So, the two main formulae for calculating composition are—

(i) **Partial Pressure = Mol fraction × Total Pressure** (3)-X

& (ii) **Per cent by volume = Mol per cent**

$$= \text{Mol-fraction} \times 100 \qquad \text{(4)-X}$$

$$= \frac{\textbf{Partial Pressure}}{\textbf{Total pressure}} \times \textbf{100} \qquad \text{(5)-X}$$

These equations are very useful for calculations involving gaseous mixtures and should be memorised.

EXAMPLE 3. *Air contains 23 per cent oxygen and 77 per cent nitrogen by weight. Calculate the percentage by volume.*

Mols oxygen $= 23/32 = 0.72$; Mols nitrogen $= 77/28 = 2.75$

Mol fraction of oxygen $= 0.72/(0.72 + 2.75) = 0.208$; mol fraction of nitrogen $= 2.75/(0.72 + 2.75) = 0.792$.

Per cent oxygen (by volume) $=$ mol per cent $=$ mol fraction $\times 100$

$$= 0.208 \times 100 = 20.8$$

Per cent nitrogen (by volume) $= 0.792 \times 100 = 79.2$.

EXAMPLE 4.—*Chlorine (at. wt. 35·46) is a mixture of the two isotopes, viz., $^{35}Cl_2$ and $^{37}Cl_2$. Calculate the percentage by volume of the former, assuming the at. wt. of isotopes to be exact whole numbers in the chemical scale.*

If the weight fraction of $^{35}Cl_2$ is x, we have

$$x \times 35 + (1-x)\,37 = 35.46 \text{ or, } x = .77$$

∴ Mol-fraction of $^{35}Cl_2 = \dfrac{x/35}{x/35 + (1-x)/37} = .7796$

∴ Percent by volume $=$ Mol per cent $= .7796 \times 100 = 77.96$

Experimental Determination of Partial Pressure—The law of partial pressure can be easily tested by mixing up known amounts of gases and comparing whether the actual pressure observed is equal to the pressure as calculated above. But, given a mixture of gases of unknown percentage composition it is a difficult affair to determine the partial pressure of each of the components. Van't Hoff has pointed out that this is possible if we can find out a membrane which is perfectly permeable to only one of the components of the mixture. This is not usually experimentally realisable except in the case of hydrogen, which is known to be thoroughly permeable to heated palladium.

Fig. 49—Partial Pressure of Gases.

The following very instructive and interesting experiment due to Ramsay illustrates such a method of determining the partial

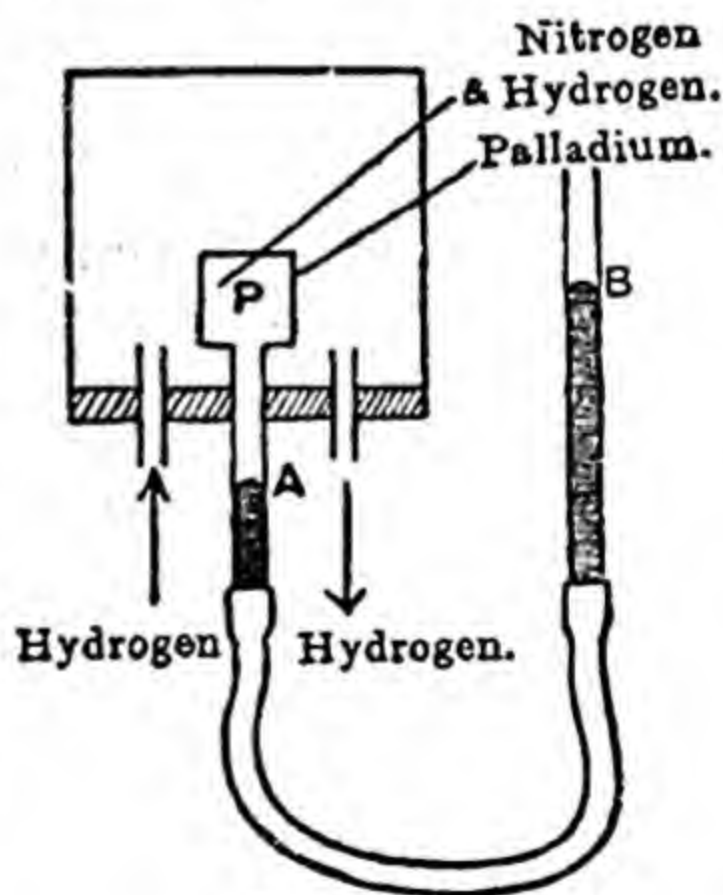pressure. P (Fig. 49) is a palladium bulb containing a mixture of nitrogen and hydrogen. It is capable of being heated and is connected to a manometer. It is surrounded by an outer bulb through which a stream of hydrogen at atmospheric pressure is passed. When the palladium bulb is heated, its walls become permeable to hydrogen but not to nitrogen and therefore, the pressures of hydrogen inside and outside become equal. The pressure indicated by the manometer will, therefore, be one atmosphere plus the partial pressure of nitrogen inside. So, the partial pressure of nitrogen becomes known, the original total pressure of the mixture is known, and hence, the original partial pressure of hydrogen is obtained by difference. The experiment demonstrates clearly the utility of *semipermeable membranes* and will be again referred to in osmotic pressure experiments.

B. SOLUTION OF GASES IN LIQUIDS

Solubility of Gases—Gases are to a more or less extent soluble in liquids. The oxygen of the atmosphere which is dissolved by water of rivers and seas is responsible for the respiration of fish and other aquatic animals.

For purposes of comparison, the amount of a gas dissolved by a liquid is expressed in terms of solubility, which *is defined as the volume of gas dissolved by 1 c.c. of the solvent at the pressure and temperature of the experiment.* Bunsen however, introduced the term absorption co-efficient which *is defined as the volume of gas in c.c. reduced to N.T.P. which is dissolved by 1 c.c. of the given liquid at a particular temperature.*

The gases widely differ from one another in respect of their solubilities which depend on the nature of the gas and the solvent, and also on the temperature and pressure of the experiment. The following table is drawn up showing the absorption co-efficients of some common gases in water and alcohol.

SOLUBILITY OF GASES (*cc. gas/cc. solvent*)

Gas	water		Alcohol	
	0°C	25°C	0°C	25°C
Hydrogen	0·0215	0·0178	0·0693	0·0661
Nitrogen	0·0232	0·0147	...	0·1312
Oxygen	0·0489	0·0285	0·2237	0·2171
CO₂	1·713	0·759	4·44	
Ammonia	1300·0	...		
HCl	506·0			

Dependence of Solubility on the Nature of the Gas and the Solvent—There is no general law connecting the solubility of different gases in liquids. But it is generally found that those

gases which either form compounds with water e.g. NH_3, or dissolve to ionise e.g. HCl, are the most soluble in water, while those which condense easily e.g. CO_2, SO_2, etc., are fairly soluble in the common solvents and the rest which are permanent gases e.g. O_2, N_2, etc., are the least soluble of these. The solubility of permanent gases like oxygen, nitrogen, etc. in water at ordinary temperature is about one per cent by volume i.e. of the order of 1 cc. per 100 cc. water. However O_2 is more soluble than N_2 in water and so though air contains 21% oxygen, dissolved air contains as high as 34% O_2, and this of course is helpful for respiration of fish and similar aquatic creatures. When gases dissolve in a liquid there is a slight expansion of volume.

Another interesting fact is that gases are less soluble in a solution than in the pure solvent and far less so, if the solution is that of an electrolyte. For example, a half normal solution of KCl dissolves 8·8 per cent and normal solution of sodium sulphate dissolves 3·2 per cent less carbon dioxide than an equal volume of water. The reason of salt-solution dissolving less gas perhaps lies in the fact that same quantity of water in the solution is bound to the ions as water of hydration and so, does not take part in dissolving the gas. The phenomenon is sometimes referred to as *salting-out effect*.

Effect of Pressure on Solubility : Henry's law—As a result of his studies of the solubilities of different gases in various solvents, Henry (1775—1836), a co-worker of Dalton, established the relationship between the solubility and the pressure of a gas. *Henry's Law* states that *the amount of a gas dissolved by a given volume of any liquid at a constant temperature is proportional to the pressure of the gas*; or stated algebraically, $w/P = $ const., where w is the mass of the gas dissolved and P is the pressure of the gas.

SOLUBILITY OF OXYGEN

Pressure cm.	Mass of gas dissolved. per litre ; (w) gms.	$w/P \times 10^5$
76·0	0·0408	53·59
61·0	0·0325	52·28
41·0	0·2220	53·14
30·0	0·0160	53·33
17·5	0·0095	54·22

The lower the pressure and the less soluble a gas is, the more closely it follows Henry's law. Like all perfect gas laws, this law is only approximately true for real gases, and has been tested by a number of investigators; the recent determinations by Morgan (1930) are quoted above.

Alternative Statements of Henry's Law—Henry's law can also be stated in another ingenious way which involves the

volume of the gas instead of its amount. Suppose, V cc. of a gas of mass m at a pressure P is dissolved. Now if the pressure is doubled, the mass of gas dissolved will, according to Henry's law, also be doubled *i.e.* be equal to $2m$. Now, m gms of gas occupies V cc. at a pressure P; now, by Boyle's law $2m$ gms of the same will also occupy V cc. at the pressure, 2P. Therefore, the volume of gas dissolved is still V but under the increased pressure, 2P.

This can be proved algebraically very easily. We have according to gas equation, $PV = \dfrac{g}{M} RT$, or $V = \left[\dfrac{g}{P}\right]\dfrac{RT}{M}$. Now, according to Henry's law $g/P = $ constant and so, $V = $ constant.

So, we may state Henry's law in the alternative way— *The volume of a gas dissolved by a given volume of any liquid at constant temperature is independent of pressure.*

There is still a third form in which Henry's law can be stated as follows—*The ratio of the concentrations of the gas in the liquid and the gaseous phase is constant,* or stated algebraically,

$$\frac{C_1}{C_2} = k \text{ (constant)},$$

where C_1 and C_2 are the concentrations of the gas in the gaseous and the liquid phase respectively. This follows easily from Henry's law, since concentration is directly proportional to pressure. This is a generalised expression of Henry's law and holds good for distribution of any molecular species between any two phases *e.g.* iodine between water and benzene, etc.

Common Phenomena in the Light of Henry's Law— The ordinary soda water bottles contain carbon dioxide gas under pressure. As soon as the pressure is released, the liquid cannot now hold all the carbon dioxide in solution since the solubility of the gas is now less and therefore, a large part of the gas gets all at once expelled out in bubbles, imparting to it the characteristic sparkling freshness.

Divers and other under-water workers remain in vessels containing air under pressure as a result of which the gases of the air dissolve to a greater extent in the lipids (fats) of the body. This increased concentration of nitrogen in the lipid sheaths of nerve trunks produces a narcotic effect. Besides, when the diver comes up, the pressure suddenly falls and the dissolved nitrogen owing to decreased solubility as expected from Henry's law comes out in bubbles inside the body fluids which often produces dangerous effect. Hence, for high pressure work a mixture of oxygen and helium is preferred, as the latter is less soluble and more diffusible than nitrogen.

Limitations of Henry's Law—The law is obeyed fairly accurately by gases which are soluble to a small extent. For gases like ammonia, hydrochloric acid, etc. whose solubilities in

water are very large, this law does not hold good at any pressure. In such cases where large deviations are found, the real causes may be traced to formation of compounds, association or dissociation, and the law should then be properly modified. Still there are cases where the law seems to be much in defect and cannot be accounted for by the above general principles.

Variation of Solubility with Temperature —Unlike other types of solutes gases are less soluble in a liquid at a higher temperature. There are, however, some exceptions such as hydrogen and inert gases, which for a particular range of temperature behave in a way opposite to the above rule. For example, 1 cc. of water dissolves 0·0137 cc. of helium at 25°C and 0·024 cc. at 50°C, while for almost all gases the solubility generally falls off very rapidly with temperature.

If Henry's law holds good, a gas will be completely expelled out from a liquid if it is boiled in the open. There are, however, some exceptions e.g., constant boiling mixtures, which evaporate off as a whole unchanged in composition at a particular temperature ; these will be again referred to later.

C. SOLUTION OF GASES IN SOLIDS

General—The solubility of gases in a solid is highly specific depending on the nature of the solid and the gas. For example, 1 gm of silver at 800°C and 1 atmosphere pressure dissolves 0·35 cc. oxygen, and far less quantity of hydrogen, but no other gases in any measurable amount. Generally, the solubility is very small and a given solid may dissolve small quantities of one or two gases, but none others.

There are, however, cases in which a gas is highly soluble in a solid, the most noted of which is that of palladium which dissolves many times its own volume of hydrogen (about 1000 times at 0°C). This case is peculiar in that the solubility decreases with rise of temperature. It is sometimes believed that such a high solubility is due to the formation of unstable compounds.

Some solids, however, have got the peculiar property of taking up large volumes of gases, and this is generally limited to the surface of the solid. To distinguish it from the ordinary process of solution this phenomenon is termed *adsorption* and will be discussed in details later in Part IV.

D. SOLUTION OF LIQUIDS IN LIQUIDS

Mutual Miscibility of Liquids—Generally speaking, liquids which are of similar constitution are miscible with one another. Thus, water and alcohol, petroleum and paraffin, mercury and metals, etc. are miscible with each other. In general, polar liquids like water, alcohol, etc.—which are associated, form ionising

solvents and have high dielectric constants,—form a class by themselves which are miscible with one another; while non-polar liquids of the saturated paraffin group—which have no residual electric field about their molecules, are non-associated and form non-ionising solvents—form a separate class by themselves and do not mix up with the liquids of the other class. The above two classes are the two extremities of classification and all types of liquids intermediate between these two limits exist.

As regards mutual solubility, three classes of liquid pairs exist:—(*i*) *The liquid pairs which are completely miscible with each other in all proportions,* viz. water—alcohol, water—sulphuric acid, etc., (*ii*) *The liquid pairs which are only partially miscible with each other,* viz. ether-water, phenol-water, alcohol-kerosene, aniline-hexane, etc. and (*iii*) *Liquid pairs which are practically immiscible,* viz. mercury—water, nitrobenzene—water, etc. It may be pointed out that "practically immiscible" does not mean zero solubility and even in the very unlike pair mercury-water the mutual solubility is measurable and in fact, mercury dissolves to the extent of about 3×10^{-7} mol per litre at 25°C.

Partially Miscible Liquid Pairs —Partially miscible liquid pairs furnish some very interesting behaviour and a few typical systems will be considered.

(*a*) **The system, Phenol : Water** —If some liquid phenol is gradually added to water, it dissolves giving a homogeneous solution until the water gets saturated when on further addition two immiscible phases separate. The lower layer is a saturated solution of water in phenol (phenol phase) while the upper layer is a saturated solution of phenol in water (aqueous phase). At a given temperature, the compositions of these two layers are of course, fixed. If more phenol is added, no change in compositions of the two layers occurs, the only change being an increase in volume of the lower layer and a decrease in volume of the upper layer. This goes on with further additions of phenol until the upper layer vanishes and only the lower layer remains, which is simply a saturated solution of water in phenol.

The temperature-composition diagram of such a system is shown in Fig. 50. Corresponding to each temperature there are two points on the diagram one representing the composition of the aqueous phase (y) and the other that of the phenol phase (z). Any horizontal line cuts the diagram at two points, giving the compositions of the two phases which are in equilibrium with each other at that temperature. yz is such a line and y and z are the compositions of the two phases respectively. The line y z is called a *tie-line*. These two compositions approach each other with rise of temperature and ultimately become equal at d (68·4°C), a closed curve being thus obtained. The temperature corresponding to the point d is called the C.S.T. (critical solution temperature of this

system as the system is homogeneous in any relative proportions above this temperature.
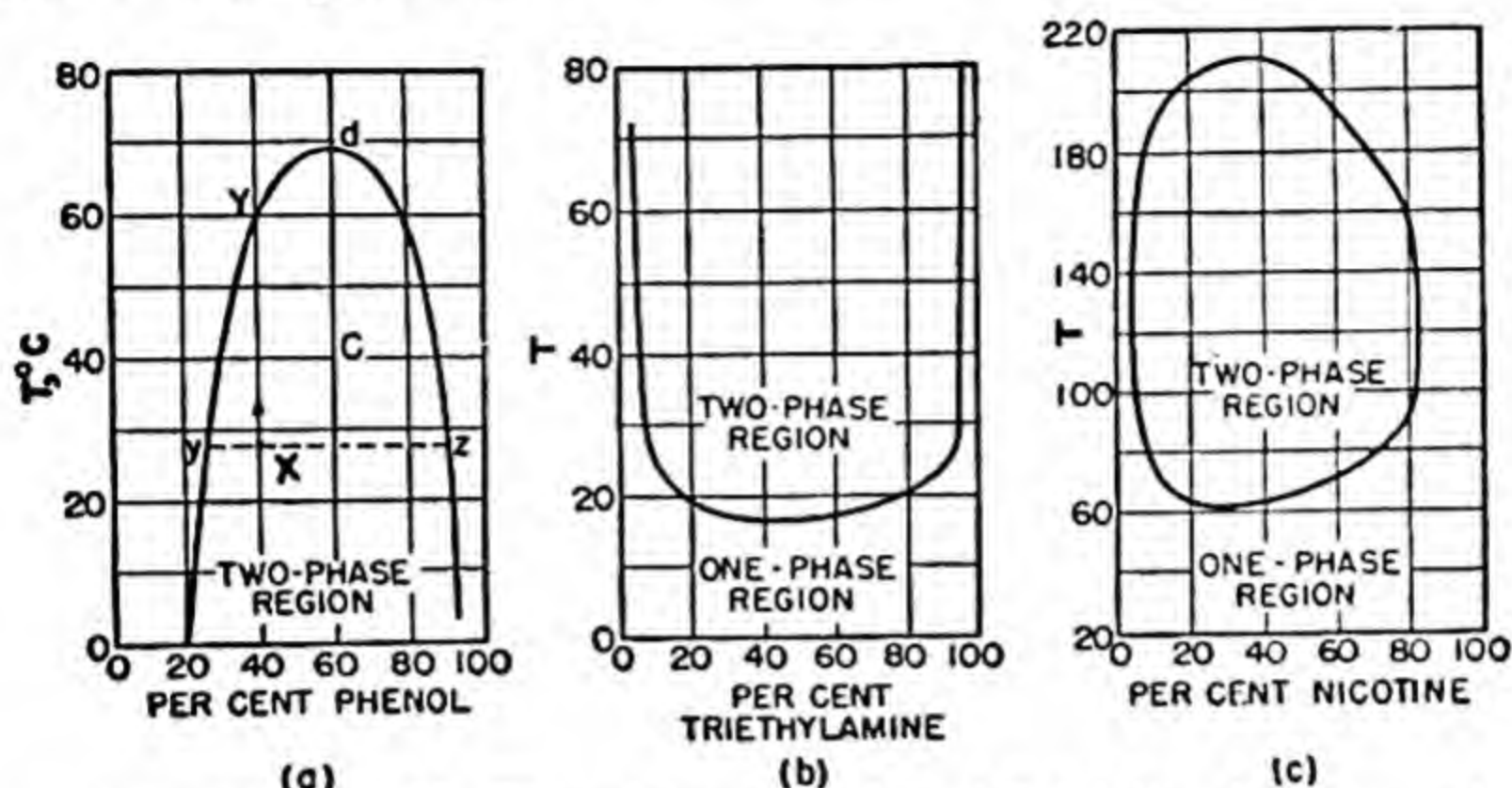
Figs. 50, 51 & 52—Three Types of Mutual Solubility Diagrams of Binary Liquid Mixtures.

(b) **The System, Triethylamine : Water** —The study of this system affords an example of the reverse of the above pheno- menon (Fig. 51). Here the two liquids are completely miscible with each other in all proportions below 18°C, but separate into two layers above this temperature. So, the curve representing the temperature and compositions of the two phases would be closed at the bottom and the lowest point would correspond to the *lower critical solution temperature*. Many amines and ethers and also methyl ethyl ketone show such behaviour with water.

(c) **The system, Nicotine : Water** —This system offers a very interesting study, as the solubility curve is a completely closed one. It has got an *upper* critical solution temperature (208°C) and a *lower* critical solution temperature (60·8°C) (Fig. 52). Between these two temperature limits the liquid pair separates into two layers, one of which is a solution of nicotine in water and the other is a solution of water in nicotine ; but outside this temperature range the two liquids are completely miscible.

An interesting fact about this system is the effect of pressure on the critical solution temperature. On increasing the pressure on the system the two critical solution temperatures approach each other ; the area of the closed solubility curve gradually decreases and finally at a high pressure it vanishes and then the two liquids become completely miscible over the whole range of temperature.

FRACTIONAL DISTILLATION

Completely Miscible Liquid Pairs —Among organic liquids complete miscibility is by far much more common than partial

get as the first condensate a liquid mixture which is richer in the more volatile component. By repeating the process a sufficient number of times each time taking the condensate as the starting material for the next distillation the final distillate may be made to approach in composition the pure more volatile component as closely as we like.

This is the principle which underlies all *fractional distillations*, the only complication being that sometimes what we have called a component in the above discussion and in the above figure (Fig. 55) may itself be a mixture in fixed proportion of the two or more basic constituents corresponding in composition to the extremum points, M or M' (called azeotropic mixture, *see later*). Thus, the more volatile component itself may be a mixture of constant composition, M (azeotropic mixture). Further, instead of condensing a portion of the vapour and redistilling it in batches as discussed above, this is automatically done very efficiently by using *fractionating columns* as to be explained in the next section.

Distillation of Liquid Pair of Type I—The theory can be easily understood with respect to its liquid-vapour equilibrium diagram on a P-X graph (Fig. 56). Here, A and B are the two components of which B is the more volatile (*i.e.* has higher vapour pressure) as shown in the graph. PP_1Q is its vapour pressure-composition curve (P-X curve) which is of course a smooth line joining the points P and Q, the vapour pressures of the two components, A and B respectively. For an ideal solution (*vide* Ch. XIII) this should be a straight line but usually this is slightly curved.
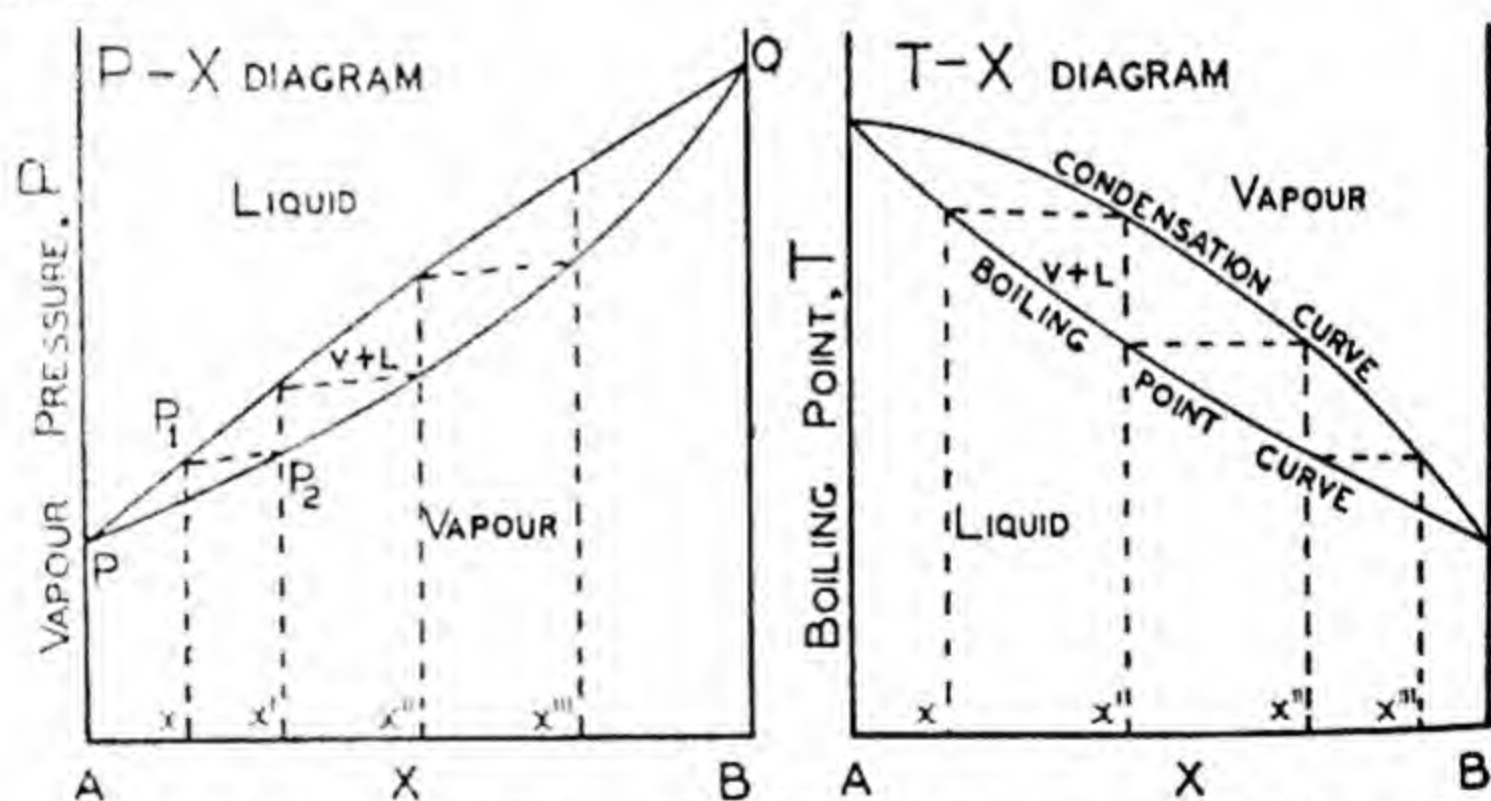
Figs. 56 & 57—Liquid-Vapour Equilibrium Diagram on a P-X graph (Fig. 56) and on a T-X graph (Fig. 57).

On the same graph is PP_2Q, the vapour composition curve. This is drawn such that any horizontal line P_1P_2 shows the composition of the liquid x and that of the corresponding vapour x' with which it is in equilibrium. It is to be noted that x' is richer in B in agreement with the fact that the vapour is richer in the more volatile constituent.

Suppose we start with a liquid of composition x. The first distillate would be of composition x'. If this x' is now submitted to redistillation, the composition of the first portion of the new distillate will be x''. It is thus evident that by repeating the process a sufficient number of times we can come as close to pure B as we like and hence, by fractional distillation on the above principle we can ultimately distil off pure B. Thus, a more or less complete separation of A and B is possible.

Use of Fractionating Columns —There are of course great practical difficulties in experimentally carrying out the step by step distillation with initial fractions of the distillate as envisaged above. This is however done automatically by the use of fractionating columns. In fractionating columns the vapour is condensed a number of times in its upwards passage and thus, a downward stream of condensed liquid meets an upward stream of vapour which in effect produces the same results as repeated condensation and redistillation of small quantities as discussed in the previous para. With a properly designed fractionating column some typical ones of which are shown in Fig. 58, under proper conditions of working, a practically complete separation of the two components is thus possible in this case. In industrial practice, well-designed metallic very big fractionating columns are used and they are generally known as *rectifying columns* and the plants as *rectifying stills*.

Liquid-vapour T-X Diagram (Type I)—The same results can as well be understood with reference to liquid-vapour equilibrium diagram on a T-X graph as shown in Fig. 57. The arguments are exactly similar except that the T-X curves are reverse of the P-X curves because, as already explained, higher vapour pressure means lower boiling point, and so no separate discussion on the basis of T-X diagram will be given here as also for the other types in later sections.

Fig. 58—Typical Fractionating Columns.

Distillation of Liquid Pair of Type II (Minimum B.P. Mixtures) —Here the vapour pressure curve shows a maximum, M. Since the maximum vapour pressure means greatest volatility i.e., minimum boiling point, we may regard any composition, as a mixture of the minimum boiling point composition, M and either of the pure components (A or B as the case may be). Looked at from the standpoint of vapour pressure curves such systems will be a

11

combination of two vapour pressure diagrams of the previous type. One portion will be in effect a P-X diagram of pure A and M, and the other of M and pure B, the composition M being
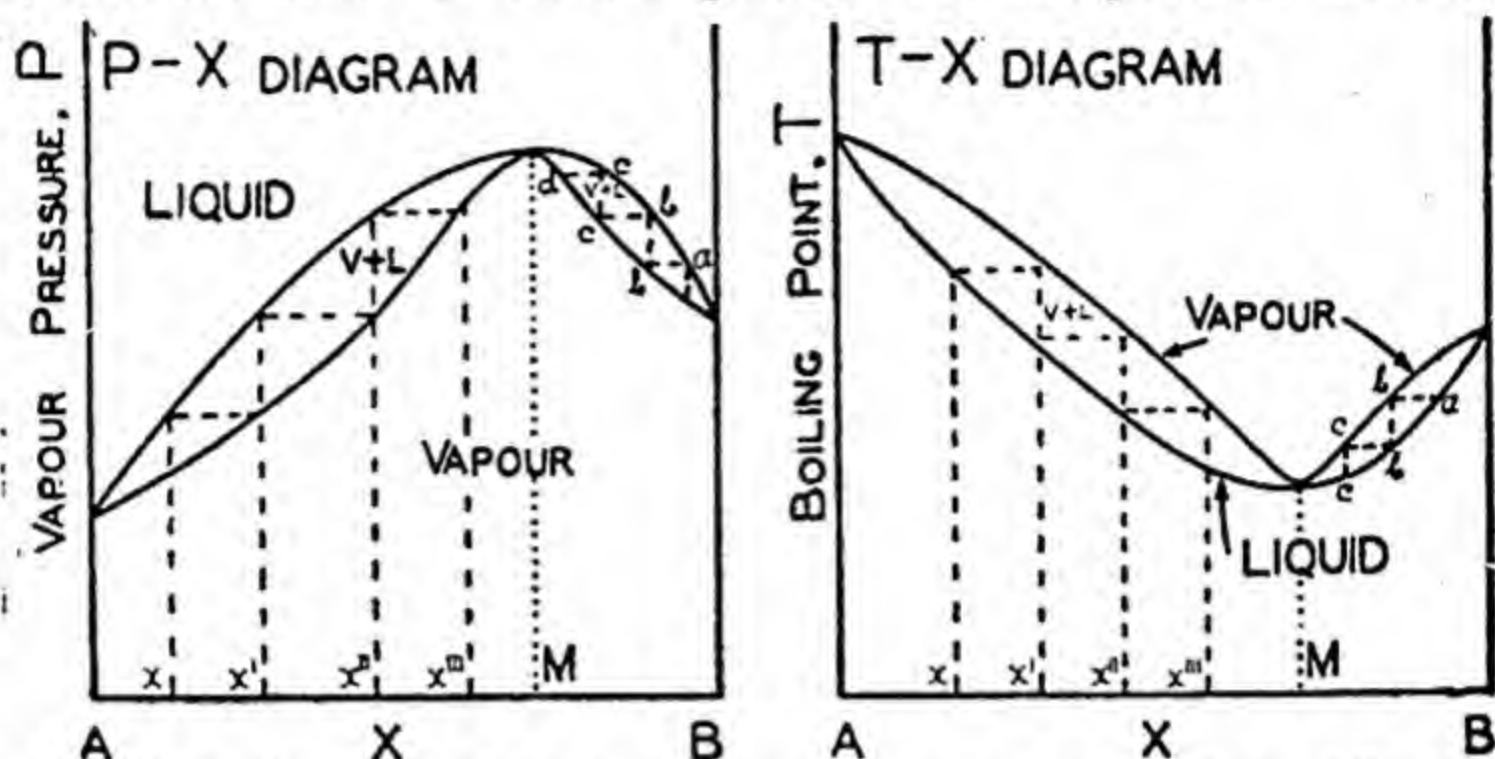

Fig. 59 & 60—P-X and T-X curve of Minimum Boiling Point Mixtures

virtually equivalent to a pure component, and of course, is the more volatile constituent in both the cases, as shown in Fig. 59. The corresponding T-X diagram (Fig. 60) would evidently be similar but upside down, and would lead to the same conclusions.

So, on submitting any mixture of this type to efficient fractional distillation the most volatile mixture, M will pass off first leaving either pure A or pure B in the still depending on whether the original composition lay between A and M, or between M and B respectively. It would, therefore, be impossible to separate the two pure components by fractional distillation. The only thing possible is to separate it into the minimum boiling point mixture and only one pure component.

The occurrence of such a pair of liquid mixture is very common in the realm of organic solvents. Ethyl alcohol-water system is an example of this type, forming a mixture of minimum boiling point, 68·13°C, which contains 95.59 per cent alcohol. The impossibility of preparing absolute alcohol by fractional distillation only will now be understood, and, therefore, the use of lime, sodium, etc. is resorted to for preparing it in the anhydrous state.

Azeotropic Mixtures—If a composition corresponding to the minimum boiling point (M in Figs. 53, 54, 59 and 60) is boiled, the mixture will distil off unchanged in composition at a fixed temperature just like a pure compound. Such mixtures corresponding to the maximum (also minimum) in the P-X curve which distil off unchanged in composition are called *constant boiling mixtures* or *azeotropic mixtures* and any fractional distillation in which the components can form azeotropic mixture is called *azeotropic distillation*. Sometimes, to distinguish this type from the other type of azeotropes to be discussed below, such azeo-

tropic mixtures are called by the explicit name of minimum B.P. azeotropic mixtures. The following table contains data for some typical azeotropic mixtures.

Component A	B. P. of A °C	Component B	B. P. of B °C	B. P. of Azeotrope	Wt. % B
Minimum B. P. Azeotropes					
Water	100	Ethyl alcohol	78·3	68·17	96
Ethyl alcohol	78·3	CCl₄	76·7	65·1	84·1
Methyl alcohol	64·7	Chloroform	61·2	53·4	87·4
Benzene	80·2	Methyl alcohol	64·7	58·3	39·6
Acetic Acid	118·5	Toluene	110·8	105·0	66
Methyl ethyl ketone	79·6	Ethyl alcohol	78·3	74·8	40
Maximum B. P. Azeotropes					
Water	100	HCl	−80	108·6	20·2
„	100	HNO₃	86	120·5	68·0
Chloroform	61·2	Acetone	56·1	64·4	21·5
Acetic acid	118·5	Pyridine	115·5	140	47

It was sometime believed that constant boiling mixtures were definite chemical compounds formed by the union of the two component liquids. Such a view is no longer held as it is found that the composition of such constant boiling mixtures continuously varies with the external pressure at which the distillation is conducted, which is totally impossible to occur for a pure chemical compound.

Hence, though a pure liquid boils at a constant temperature, the converse of it is certainly not true. But a constant boiling mixture and a pure liquid can be easily differentiated by submitting both to fractional distillation at various reduced external pressures. In the case of the pure liquid, all fractions of the distillate as well as the residual liquid will be identical, whereas for the azeotropic mixture, these fractions may differ among themselves in properties.

Distillation of Liquid Pair of Type III—The P-X curve of this class of liquid pair shows a minimum, M' (Fig. 53) and the T-X curve shows a maximum, M' (Fig. 54). This type of mixture is much less common and so is industrially less important than the previous type of maximum vapour pressure mixture. The behaviour of such mixtures as also the corresponding curves will be just the reverse of the previous type and so its behaviour need not be discussed in detail. The liquid mixture corresponding to the composition of the minimum point, M' is the least volatile (*i.e.* has the maximum boiling point) as its vapour pressure is lower than that of any other composition. So, if any mixture is fractionally distilled the composition of the liquid remaining in the flask will gradually approach towards the composition of the point

M', for, any other mixture being more volatile will pass off first. When the composition M' has been reached the liquid will boil at constant temperature, unchanged in composition, just like a pure liquid at its boiling point. Thus, by fractional distillation of a mixture of this type we can at most separate it into a maximum B. P. mixture and a pure component. The distillation diagram on a T-X plot of an actual system of this type viz. acetone-chloroform is shown in Fig. 61.
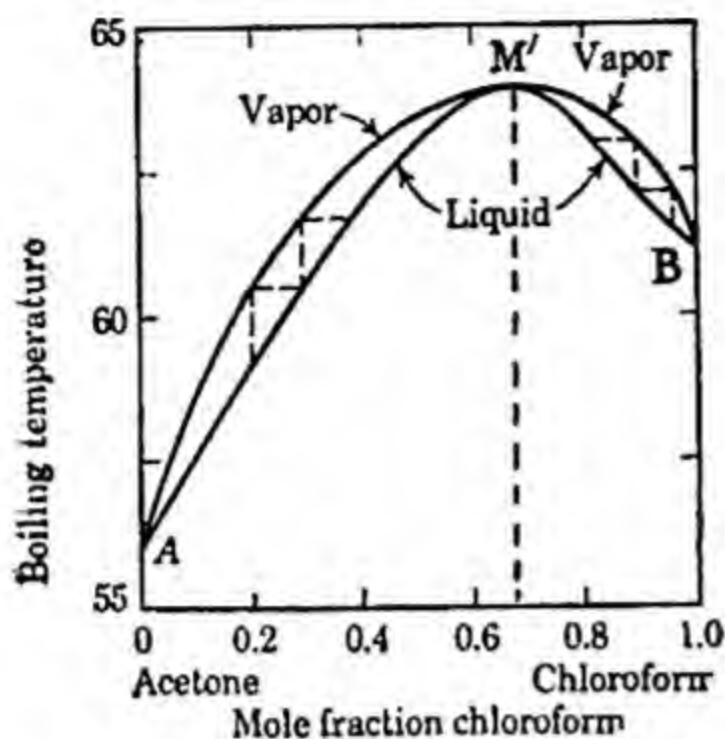

Fig. 61—T-X Diagram of Acetone-Chloroform Mixtures (Type III).

If we submit a composition corresponding to the maximum B.P. mixture evidently it will boil off unchanged. Such mixtures are also called *azeotropic mixtures* or more explicitly maximum B.P. azeotropic mixtures. Some examples are given in the foregoing table.

Examples of Maximum B.P. Systems—It needs be pointed out that only systems which show strong negative deviation from Raoult's law (Ch. XIII) may show this behaviour (Type III.). Since negative deviation from Raoult's law is shown by systems with strong mutual interaction, usually accompanied by evolution of heat and contraction in volume, we must look for such types among organic liquid pairs with strong mutual attraction. A good example is chloroform-acetone where we know that there is strong hydrogen bond (*vide* Part VI) formation, $(CH_3)_2CO$. . . $HCCl_3$, and this system belongs to this type (Fig. 61).

Sulphuric acid and water form a constant boiling mixture of this type at a concentration of 98·7 per cent of the acid, and hydrochloric acid and water, at 20·24 per cent of the acid. If a dilute solution of HCl is boiled, the vapour coming out is richer in water and the mixture remaining in the flask gets concentrated. On the other hand, on boiling a concentrated solution of HCl the vapour leaving the system is richer in HCl and the liquid left gradually falls in concentration. In any case on continued boiling this change in concentration goes on until a 20·24 per cent composition is reached, when the mixture boils off unchanged in composition at a fixed temperature. The composition of the constant-boiling HCl-water mixture is so remarkably constant and is so little affected by small change of atmospheric pressure that this acid is often used as standard in acidimetry.

Industrial Importance of Constant Boiling Mixtures (Azeotropic Distillation) —The tremendous development of lacquers, varnishes and other similar products during recent years has neces-

sitated large scale production of a large number of organic solvents which in their turn, oftentimes, involve fractional distillation of solvent mixtures produced by various processes. Sometimes, very ingenious methods are applied to overcome the difficulties of separation of the pure components. An apt example is the German method of manufacturing absolute alcohol from ordinary alcohol. As already pointed out water and alcohol form a constant boiling mixture which prevents the purification of alcohol by ordinary fractional distillation to more than about 96 per cent. Distillation with lime may increase the purity of alcohol to 99·2 to 99·9 per cent, but it is extremely difficult to get rid of the last traces of water.

It has been observed that alcohol, water and benzene form a ternary constant boiling mixture in the proportion 18·5 : 7·4 : 74·1 which boils at 64·85°C—a temperature about eight degrees lower than the boiling point of alcohol. The calculated amount of benzene is added to the alcohol containing traces of water and the mixture is submitted to fractional distillation. The first portion to boil off is the ternary mixture of benzene, alcohol and water, and the second fraction, a binary mixture of any excess benzene with alcohol (B. P. −68·1°C); the residual liquid in the still is absolute alcohol. Since the benzene is used for the purpose of carrying off the last traces of water, it is termed an 'entrainer' for water. The solvent industry is so highly developed nowadays that such azeotropic distillations have been the standard practice in their manufacture.

Distillation of Partially Miscible and Immiscible Liquids—It can be proved on theoretical grounds, that the vapour pressure of a system consisting of two separate liquid phases is constant at constant temperature. Thus, the boiling point of such a system consisting of two partially miscible or immiscible liquids is constant and is lower than the boiling point of either of the pure components. Also, for immiscible liquid pairs, the composition of the vapour phase is constant and the amount of each of the components present is proportional to their respective vapour pressure at the boiling point of the mixture. Thus a mixture of aniline (B.P.—184·4°C) and water would boil at a temperature below 100°C, and as long as there are both aniline and water present (made possible by supplying steam to the mixture) the vapour coming out would contain both aniline and water in proportion to their respective partial pressures at the temperature of boiling. Benzaldehyde (B.P.—178°C) also behaves similarly being volatile in steam and the distillate contains 31·4 per cent. benzaldehyde.

The ratio of the weights of the two liquids in the distillate can be readily calculated. Suppose the partial pressure of water at the boiling point of the mixture be P_1, and let V be the total volume of vapour distilled out. Then

$$P_1 V = n_1 RT = \frac{g_1}{M_1} \times RT \text{ or } P_1 M_1 = g_1 \times \frac{RT}{V};$$

If the other component, aniline has a vapour pressure, P_2 at the boiling point of the mixture, then

$$P_2 V = n_2 RT = \frac{g_2}{M_2} \times RT \text{ or } P_2 M_2 = g_2 \times \frac{RT:}{V}$$

where M_1 and M_2 are the molecular weights and g_1 and g_2 are respectively the weights of the components present in the distillate.

Therefore, dividing one equation by the other we get,

$$\frac{g_1}{g_2} = \frac{P_1 M_1}{P_2 M_2} \qquad \cdots \qquad \cdots \qquad \cdots \quad (6)\text{-XI}$$

i.e. the ratio of the weights of the substances distilling is the ratio of the products of their respective partial pressure and molecular weight; hence a high boiling point *i.e.* low vapour pressure is counterbalanced by a large molecular weight. Thus the main condition of a substance being amenable to steam distillation is that it must have sufficient vapour pressure at nearabout 100°C. In technical practice high pressure steam is often used to increase the volatility of the substance.

Example 5. *A mixture of nitrobenzene and water boils at 99°C. Calculate their respective weights in the distillate.*

From the table, vapour pressure of water at 99°C. is 733 mm. Since the liquid mixture. boils at 99°C, its total vapour pressure must be 760 mm. Therefore, the partial pressure of nitrobenzene in the vapour is 760 mm.— 733 m.m. = 27 m.m.

Now, mol. wt. of nitrobenzene is 123. and that of water is 18.

$\therefore$ according to eqn. (6) $\dfrac{\text{wt. of nitrobenzene}}{\text{wt. of water}} = \dfrac{123 \times 27}{18 \times 733} = \dfrac{1}{3 \cdot 94}$

i.e. about 1/5th of the distillate is nitrobenzene.

The above method in a reverse way may be used for the determination of molecular weight of a liquid immiscible with water.

Example 6. *It is observed that a mixture of aniline and water boils at a temperature of 98°C, at which the vapour pressure of water is 717 m.m. Calculate the mol. wt. of aniline, from the fact that the distillate contains one part of aniline to 3·23 parts of water.*

The partial pressure of aniline = 760 – 717 = 43 m.m.

Therefore, according to equation (6),

$$\frac{g_1}{g_2} = \frac{P_1}{P_2} \times \frac{M_1}{M_2}, \text{ we have } \frac{1}{3 \cdot 23} = \frac{43 \times M}{717 \times 18}$$

M_1 = 93, in good agreement with the theoretical value.

Steam Distillation —The above discussion is the principle of steam distillation—a process widely used in organic laboratories to purify immiscible organic liquids. A distilling flask contains the mixture of the two liquids, say, aniline and water, and is heated to boiling. Steam is passed through the mixture, and the distilling flask is connected to a condenser and a receiver as usual. The distillate contains water as well as aniline and can be easily separated by a separating funnel.

E. SOLUBILITY OF SOLIDS IN LIQUIDS

General—Solids have a wide range of solubility values in a given solvent from being very sparingly soluble to very highly soluble. For example, all the water present in our earth in any form is not enough to dissolve a gram of mercuric sulphide

whereas potassium iodide dissolve in less than its own weight of water. Generally inorganic salts are sparingly soluble in organic solvents and organic solids have equally poor solubility in water. Thus solubility depends mainly on the nature of the solid and the solvent and on the temperature. There is no theory which can predict the solubility of a given solid in a given liquid. It is a general rule that two substances of similar composition dissolve in each other. Very peculiarly, however, though organic simple hydroxy compounds are more or less soluble in water, heavy metal hydroxides are insoluble.

The amount of a solid which is dissolved by 100 gms of a liquid to form a saturated solution at any temperature is called the *solubility* of the solid in that liquid at that particular temperature. But, for physico-chemical purpose it is more convenient to express the solubility in molarity, molality or mol-fraction.

It is a peculiar fact that the solubility of a solid depends to some extent, on its fineness of subdivision. Ordinary gypsum dissolves to the extent of 2·080 gms of $CaSO_4$ per litre of water at 25°C, whereas if the gypsum is very finely powdered. an aqueous solution of it may contain as much as 2·552 gms $CaSO_4$ per litre. This has an important bearing on the methods of quantitative analysis. The precipitate of, say, barium sulphate, first formed is too fine to be retained by filter papers, but on digestion of the precipitate for a few minutes at nearabout boiling temperature, the precipitate does no longer pass through the filter. The explanation of this is that the fine particles are more soluble than the coarser ones, and so dissolve in the liquid and get precipitated on the coarser ones; as a result the finer ones are destroyed whereas the less fine ones grow in size and ultimately become sufficiently coarse to be retained in the pores of ordinary filters. Warming the solution only hastens the change. This is very similar to smaller rain drops disappearing and the bigger rain drops growing at the cost of the smaller ones.

Variation of Solubility with Temperature —The solubility curves of certain solids are shown in the accompanying diagram (Fig. 62), where the temperature has been plotted as the abcissa and the solubility as ordinates. The solubility of most solids *increases* with *rise of temperature* as would be seen by the solubility curves of KNO_3, KCl, etc. The solubility curve of common salt is slightly peculiar, since it runs almost *parallel* to the temperature axis, thus indicating very little increase of solubility with rise of temperature. Some salts, however. notably some calcium compounds *e.g.* $Ca(OH)_2$, $CaSO_4$, $CaCrO_4$, Ca-acetate, Ca-butyrate, cerous sulphate $(Ce_2(SO_4)_3)$, etc. show a *decrease* of solubility *with rise of temperature*. (For heat of solution from solubility data see P. 118).

The solubility curves so far discussed are smooth curves, but there are some salts, *e.g.* ammonium nitrate, sodium sulphate, etc. whose solubility curves show a sudden change in direction. From the figure it would be seen that the solubility curve of sodium sulphate is smooth up to 33°C, where it suffers a sharp change in direction. The explanation of this peculiar behaviour is that the initial branch of the curve represents the equilibrium

between sodium sulphate solution and solid sodium sulphate decahydrate ($Na_2SO_4, 10H_2O$). The latter part of the curve is the solubility curve of unhydrated sodium sulphate and the point,
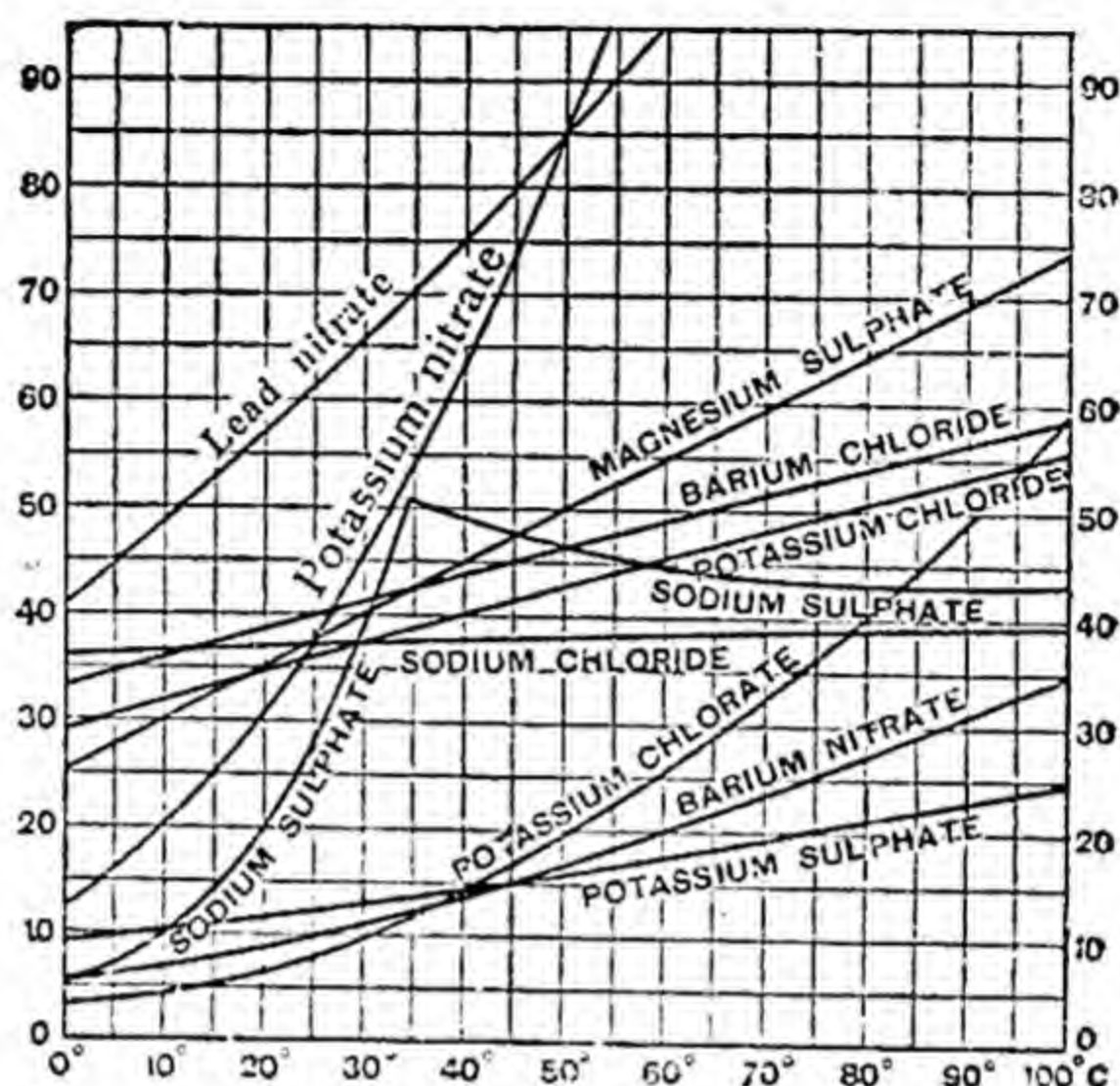

Fig. 62—Solubility Curves of Solids

where the sudden change in direction occurs, is the point of intersection of the two curves. Thus, 33°C is the *transition temperature* between the decahydrate and un-hydrated sodium sulphate.

Distribution of a Solid between Two Liquids —Suppose to a dilute aqueous solution of oxalic acid is added some quantity of ether and the whole is thoroughly shaken up and allowed to settle. Two layers will then separate, the upper one being of course, the ether layer. Now, oxalic acid is soluble both in ether and in water and hence, it will be present in both the layers, *i.e.* oxalic acid will be distributed between the two layers. Such a distribution takes place whenever a solute is shaken up with two immiscible solvents, in each of which the solute dissolves, *e.g.* iodine in water and chloroform, acetic acid in water and ether, etc. Nernst carried out numerous distribution experiments and expressed his results in the shape of the following law. If a solute is shaken up with two immiscible liquids, in both of which the solute is soluble, the solute distributes itself between the two liquids in such a way that *the ratio of its concentrations in the two liquid phases is constant independent of the amounts of the solid or the solvents*; or, stated mathematically,

$$\frac{c_1}{c_2} = K \qquad \qquad \qquad \dots \text{(17)-XI}$$

where c_1 and c_2 are the concentrations of the solute in the two phases respectively and K is a constant called distribution co-

efficient or **partition co-efficient.** This law is called the Nernst's distribution law, and Henry's law for gases is a special case of it. This law is only valid if no association, dissociation or chemical combination between the solute and the solvent takes place.

This law has been experimentally verified in a number of cases and is found to hold good only approximately like Henry's law. The data for the distribution of iodine between carbon disulphide and water is given in the table, where $c_1 : c_2$ is found to remain fairly constant.

DISTRIBUTION OF A SOLUTE (*Partition Law*)

Iodine between CS_2 and water at 18°C			Benzoic acid between benzene and water at 20°C.			
Gms. iodine in 10cc. water (c_2)	Gms. I per 10cc. $cs_2(c_1)$	$K = \dfrac{c_1}{c_2}$	conc. in water (c_1)	conc. in benz. (c_2)	c_2/c_1	$\sqrt{c_2}/c_1$
0·0041	1·74	420	0·0075	0·0084	1·12	12·3
0·0032	1·29	400	0·0125	0·0239	1·92	12·4
0·0016	0·66	410	0·0210	0·0651	3·10	12·2
0·0010	0·41	410	0·0327	0·1650	5·05	12·4

If the molecular weight of the substance is not the same in the two liquids *i.e.* if molecular association has occurred in any of the liquids, this simple law will not hold good. If the molecular complexity has increased n times in the second solvent, it can be proved from the law of mass action that the equation will take the form $c_1 : \sqrt[n]{c_2} = K$. From the table for the distribution of benzoic acid between benzene and water it is found that the ratio $c_1 : \sqrt{c_2}$ is constant showing that benzoic acid exists as double molecules in benzene.

These equations are useful in calculating the amount of a solute which can be extracted out from a given solution by another solvent as illustrated for a simple case by the following example.

Example 7. *The distribution constant of succinic acid between water and ether is 5·5 ; 100 c.c. of normal succinic acid is shaken with 50 c.c. of ether. Find the resulting concentration of the ether and the water layer.*

100 c.c. N succinic acid contains 5·9 gms. of acid

Let x gms. of the acid dissolve in the ether layer.

∴ conc. of ether layer $= (x/50) \times 1000$ gms. per litre $= 20x$

∴ conc. of water layer $= (5·9 - x) \times 10$ gms. per litre.

$$\frac{C \text{ water}}{C \text{ ether}} = \frac{(5·9 - x) \, 10}{20x} = 5·5 \text{ or, } x = 0·49$$

∴ conc. of ether layer $= 0·49 \times 20 = 9·8$ gms. per litre ;

∴ conc. of water layer $= 5·41 \times 10 = 54·1$ gms. litre.

It can be proved on theoretical grounds that the partition co-efficient is also equal to the ratio of the solubilities of the solute in the two solvents. Hence, the partition co-efficient,

$$K = \frac{c_1}{c_2} = \frac{s_1}{s_2} \dots \qquad \dots \qquad \dots \quad (8)\text{-}XI$$

where s_1 and s_2 are the solubilities of the solute in the two immiscible liquids. From this relation it is possible to calculate either the partition co-efficient from solubility data or the solubility from distribution experiments.

A very interesting application of liquid—liquid equilibrium is made in the modern process of refining lubricating oil. The crude lubricating oil contains some undesirable constituents of a highly aromatic structure, which easily get oxidised into acids, form sludge and corrode the engine. They are, however, more soluble in various solvents and in actual industrial plants liquid sulphur dioxide (at times mixed with benzene) is used as the extracting solvent. A slightly different type of application is the liquid—liquid extraction of a turpentine or benzene solution of dark coloured rosin by furfural for extracting out the colouring matter to prepare a pale rosin of high quality.

For an application of distribution experiments to determine the $KI + I_2 \Longleftrightarrow KI_3$ equilibrium, *vide* Part III (Ch. XVII).

Example 8. *If m_0 gms of a solute are present in V_1 litres and the solution is extracted using V_2 litres of an immiscible solvent each time, calculate the amount of the solute remaining after n extractions, given the distribution constant is $K\ (= C_2/C_1)$.*

Let m_1 be the amount of solute remaining after the first extraction. Then the concentration in the first layer is m_1/V_1, and the concentration in the second layer is $(m_0 - m_1)/V_2$. Hence, according to Nernst law,

$$\frac{(m_0 - m_1)/V_2}{m_1/V_1} = K \text{ or } m_1 = m_0 \left(\frac{V_1}{V_1 + KV_2} \right)$$

Now let m_2 be the amount of solute remaining after the second extraction. The relationship between m_2 and m_1 must be the same as that between m_1 and m_0. Hence,

$$m_2 = m_1 \left(\frac{V_1}{V_1 + KV_2} \right) = m_0 \left(\frac{V_1}{V_1 + KV_2} \right)^2$$

and similarly, if m_n be the amount left after the n-th extraction, then,

$$m_n = m_0 \left(\frac{V_1}{V_1 + KV_2} \right)^n$$

F. SOLID SOLUTION

If a solution of iodine in benzene is cooled, the solid which separates is neither pure benzene nor pure iodine but is a homogeneous mixture of the two. The composition of the separating solid continuously varies with the composition of the solution. Such *homogeneous* mixtures of solids are called *solid solutions*. Solid solutions are frequently met with in cases of metallic alloys. Thus gold and silver form alloys in all proportions which are really soild solutions consisting of the two compounds. Similarly, brass is a solid solution of copper and zinc.

Almost all metallic alloys are solid solutions of the component metals, or a mixture of two or more solid solutions. In the latter case, any surface of the alloy on etching or breaking will appear non-homogeneous under a microscope.

EXERCISES

1. How does the solubility of a gas depend on the temperature and pressure? State Henry's law in all the ways possible and discuss its limitations.

2. Explain what is meant by :—(a) Solid solution, (b) critical solution temperature, (c) partition co-efficient, (d) constant boiling mixture is not a definite chemical compound, (e) distillation in steam (f) constant boiling mixture, and (g) partial pressure.

If M is the average mol. wt. of a mixture of gases, prove that $PV = (g/M) RT$.

3. Discuss fully the methods you would use to separate the components of a binary liquid mixture. State the limitations. Illustrate with examples and sketches of the apparatus employed.

4. What will be observed with regard to temperature and composition of the contents of three separate flasks containing respectively water, dil. HCl and dil. NaCl solution, if they are gradually heated.

5. If water containing dissolved nitrogen is boiled, the dissolved gas is completely expelled out. If HCl gas is dissolved in water and the solution is boiled, something quite different happens. Describe and discuss what happens in the latter case.

6. Express the concentration of the following solutions in (a) molarity and normality, (b) molality, (c) mol-fraction and (d) percentage by weight :—

(i) 4·38 gms. $CaCl_2$ are present in 52·3 cc.; density of the solution = 1·12; (ii) a mixture of 50 c.c. alcohol (density = ·8) and 50 c.c. water : the total volume of the mixture = 92 cc.

[(i) ·7546 molar; 0·3773 normal; 0·728 molal; mol-fraction of calcium chloride 0·0129], (ii) conc. of alcohol = 9·43 molar, 17·4 molal, and 0·238 mol-fraction.

7. A sample of water contains 1 per cent heavy water (D_2O) by weight. Calculate the mol per cent. of heavy water in it. [5·26]

8. Ten grams of benzene are mixed with 96 grams of toluene and the resulting solution is 0·870 times as heavy as water. Calculate the concentrations of both benzene and toluene in molarity and mol per cent.
[Benzene :—1·055 mol/litre, 10·94; Toluene—8·61 mol/litre, 89·12]

9. 1 gm. of electrolytic gas is contained in a volume of 1 litre at 27°C. Calculate the partial pressures of hydrogen and oxygen.
[1·37 atmos; 0·68 atm.]

10. 1 gm. of oxygen, 1 gm. of hydrogen and 1 gm. of methane are mixed and put in a vessel under a total pressure of 1 atmosphere. Calculate mol. fraction, partial pressure and conc. in mols per litre of each gas.
[0·053, 0·842, 0·105]

11. Explain the principle underlying the process of steam distillation.

A mixture of water and nitrobenzene is distilled at one atmosphere by passing through it a current of steam. Calculate the per cent by weight of nitrobenzene in the distillate given that the vapour pressure of water at 100°C is 760 m.m. and changes by 4·47% per degree whereas that of nitrobenzene at 100°C is 20·8 m.m. and changes by 5·20% per degree.
[$p_1 = 20·16$ mm, $p_2 = 739·8$ mm, $w_1/w_2 = 0·1863$, 15·7%]

12. The partition co-efficient of iodine between water and CS_2 is 0·0017. An aqueous solution of iodine containing 0·1 gm of iodine per 100 c.c. is shaken with CS_2. To what value does the concentration of the aqueous solution sink (a) when a litre of it is shaken with 50 c.c. of CS_2, (b) when a litre of it is shaken successively with five separate quantities, 10 c.c. each of CS_2?   [·0329 gm/l, 6·479×10⁻⁵ gm/l].

13. Explain what is meant by the distribution law for a substance between two immiscible solvents. Show its relation to Henry's Law regarding the solubility of gases in liquids.

Calculate how much succinic acid would be extracted from 100 c.c. of water containing 5 gms. of the acid if extracted with 50 c.c. of ether. The partition co-efficient of succinic acid between water and ether is 5·5.
      [0·417 gms]

14. The partition co-efficient of a substance between chloroform and water is approximately 5 : 1. Compare the quantities of the substances extracted from 100 c.c. of an aqueous solution by 100 c.c. of chloroform using (a) all the chloroform at a time and (b) using the chloroform in two instalments using 50 c.c. at a time.   [5 : 5·51]

15. Prove assuming the formula deduced in example 7. that the amount extracted by two extractions with equal volumes of solvent is always greater than that extracted in one single extraction using the total volume at a time.

16. If a solution is extracted repeatedly with an immiscible solvent using the same volume of the latter each time, show that the logarithm of the residual concentration plotted against the number of extractions would give a straight line.

PHYSICAL CHEMISTRY OF DILUTE SOLUTIONS

I. Osmotic Pressure

Osmosis—All solutions exhibit an important behaviour of great physicochemical interest, called osmosis. Suppose we insert between a solution and a solvent a membrane, which does not allow the solute molecules to pass through but allows free passage to the solvent molecules. Such a membrane which allows the solvent to pass through preferentially but precludes the passage of solute molecules through it, is called a **semipermeable membrane.** Examples of such membranes of more or less efficiency are fish bladders, lining of egg shells, cellophane paper, parchment, collodion, many inorganic precipitates (jellies), *e.g.*, copper ferrocyanide, calcium phosphate, copper silicate etc., and also various other membranes present in biological systems.

Since the ideal semipermeable membrane allows only the solvent to pass through and not the solute at all, the solvent will flow through the membrane towards the solution and will tend to dilute it. The same phenomenon would take place if we had separated two solutions of unequal concentrations with a semipermeable membrane, but here the net flow of the solvent would take place from the lower to the higher concentration tending to equalise the two concentrations. *This spontaneous passage of solvent from a solution of lower concentration towards a solution of higher concentration when the two are separated by a semipermeable membrane is called osmosis.*

It should be very carefully noted that if the semipermeable membrane is not present in the above set-up, the solute would diffuse from the region of higher concentration to the region of lower concentration until the concentration becomes uniform throughout. This phenomenon is called *diffusion.* On the contrary, in the case of osmosis, the solvent moves in the reverse direction viz., from the dilute towards the concentrated solution. The ultimate result, however, is *the same in both the cases*, viz., an equalisation of concentration throughout all accessible region.

Abbé Nollet's Experiment.—Osmosis *i.e.* passage of a solvent through membranes was first observed by Abbé Nollet (1748). Abbé Nollet used an animal membrane (pig's bladder) as the semipermeable membrane, which was stretched across the mouth of a thistle funnel, P (Fig. 63). The funnel was filled with a strong sugar solution, S, and inverted over a trough of water, W, as shown in the figure. The water gradually rises in the stem of the thistle funnel and a position of equilibrium is ultimately reached when the hydrostatic pressure equalises the pressure forcing the water in. This pressure developed as a result of osmosis

is the *osmotic pressure* of the solution and is measured by the difference in water levels inside and outside.
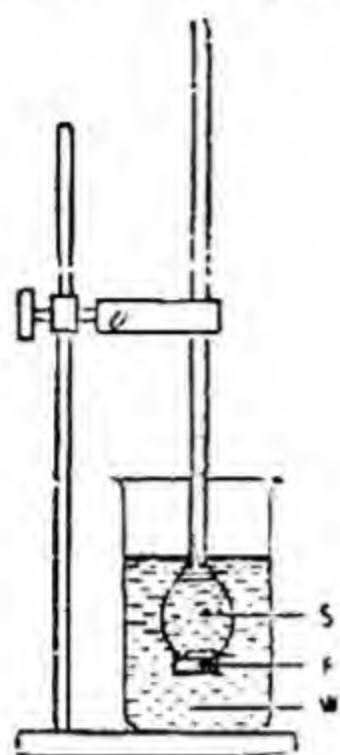

Fig. 63—Abbe Nollet's Experiment.

It should be realised that a semipermeable membrane is not the only type of selective barrier to flow of a dissolved solute, and such selective barrier may be created in other ways. But, whenever such a barrier occurs, the solvent tends to flow into the region accessible preferentially to the solute only. In fact, swelling of leather and many such phenomena are basically of a similar origin viz. restriction of a solute in its free accessibility of all region occupied by the solvent.

Definition of Osmotic Pressure. —The above experiment of Abbé Nollet affords a precise definition of osmotic pressure. Suppose, we have an arrangement as shown in the adjoining figure (Fig. 64). It is a doubly bent tube fitted with a semipermeable membrane, M on one side of which there is the pure solvent while on the other is the solution, both arms being fitted with water-tight pistons. This system cannot be in equilibrium, since the solvent will tend to pass to the solution, unless we apply a pressure P on the piston on the solution's side to counteract this tendency of the solvent to flow in. This excess pressure, P on the solution's side is the osmotic pressure of the solution at this concentration. So, we may give the following definition of osmotic pressure.
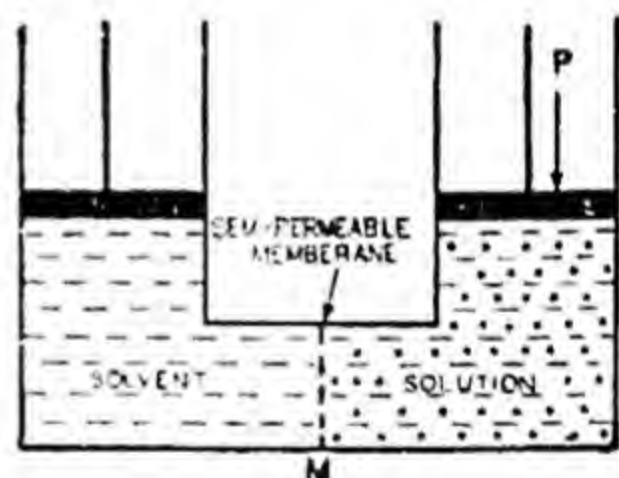

Fig. 64—Definition of Osmotic Pressure

If a solution is separated from the solvent by means of a semipermeable membrane, the excess pressure which has to be applied to the solution in order to check the inflow of the solvent and establish equilibrium in the system, is called the osmotic pressure of the solution.

The main point to realise about osmosis and osmotic pressure is that they are manifestations of the fact that a solution and a solvent (or two solutions of unequal concentrations) are not in thermodynamic equilibrium. Osmosis is merely a passage towards this equilibrium.

Experimental Determination of Osmotic Pressure. —Reliable measurements of osmotic pressure could not be made for a long

time owing to the difficulty of producing a satisfactory semi-permeable membrane. This was first surmounted by Traube (1867), who discovered after many unsuccessful attempts with membranes of various inorganic substances, e.g. Ca-phosphate, prussian blue, etc. that the chocolate-red precipitate of *copper ferrocyanide*, when supported on the walls of the pores of a porous cell acts as an ideal semipermeable membrane, which could stand very high pressure.

We owe to the botanist, Pfeiffer (1877), the first reliable quantitative measurements of osmotic pressure. His method was later on improved upon by Morse, Frazer and their coworkers (1901—23) in America. Also, Berkeley and Hartley (1906—09) in England using a different type of apparatus have produced a wealth of experimental data in this line.

Pfeiffer's Method —(*i*) *Deposition of the semipermeable membrane*:—A specially prepared earthenware porous pot after proper cleansing and drying is filled with water and left to itself until the inside pores are full of water. It is now kept immersed in a 3 per cent. solution of copper sulphate for some time, and then the interior of the pot is thoroughly washed out and quickly dried. The cell is then filled with a 3 per cent potassium ferrocyanide solution and again placed in the copper sulphate solution. The ferrocyanide gradually diffuses in and deposits a membrane inside the pores when further diffusion is prevented. After allowing sufficient time, the cell is washed and tested for various pressures. The cell is thoroughly washed free from all electrolytes and is then ready for use.

(*ii*) *Measurement of Osmotic Pressure*—The porous cup, P thus prepared is filled with the solution whose osmotic pressure is to be measured. The porous cup is cemented to a glass tube (g) which is fitted watertight with a stopper, through which passes a glass tube connecting it with a closed type air mano-meter, M (Fig. 65). The whole apparatus is placed in a tank of water kept at a constant temperature. Water gradually diffuses in and develops a high pressure. Sufficient time (some-times, weeks) is allowed to attain equilibrium, and the osmotic pressure is then read on the manometer already calibrated. It is necessary to find the change in concentration

Fig. 65—Pfeiffer's Method
(*Osmotic Pressure*)

of the solution due to the inflow of the solvent, but it is experi-

mentally found that with closed-type manometer the volume of water coming in is very small.

Morse's Method. —Morse, Frazer and their coworkers modified the method of Pfeiffer in two important respects. Firstly, they devised a method of preparing porous cells of very fine and uniform texture, so that they could make a strong membrane capable of withstanding higher pressures. Secondly, they modified the method of deposition of membrane. Their method is to take a solution of copper sulphate in the porous cell, which is partly immersed in a solution of potassium ferrocyanide and a *current* is sent in such a way that the copper ions travel outwards and the ferrocyanide ions travel inwards, so that they meet inside the pores and get deposited there as a membrane of Cu-ferrocyanide. The completion of the process is known by a marked increase in resistance, when the current almost stops. The cell is then thoroughly washed and is ready for use. Their experimental set-up is similar to that of Pfeiffer and is shown in Fig. 65. For measurement of pressure Morse used a manometer filled with nitrogen. Later workers introduced more refined methods such as an electric resistance gauge and later, water interferometer, the pressure being indicated in the former by a change of electric resistance of a wire and in the latter by the variation of the refractive index of water.

Berkeley and Hartley's Method —An important improvement in the method was devised by Earl of Berkeley and E. G. J. Hartley (1909). Instead of allowing water to diffuse in and develop its own osmotic pressure, they balance the inflowing tendency of the water by an applied external pressure which by definition, is equal to the osmotic pressure.
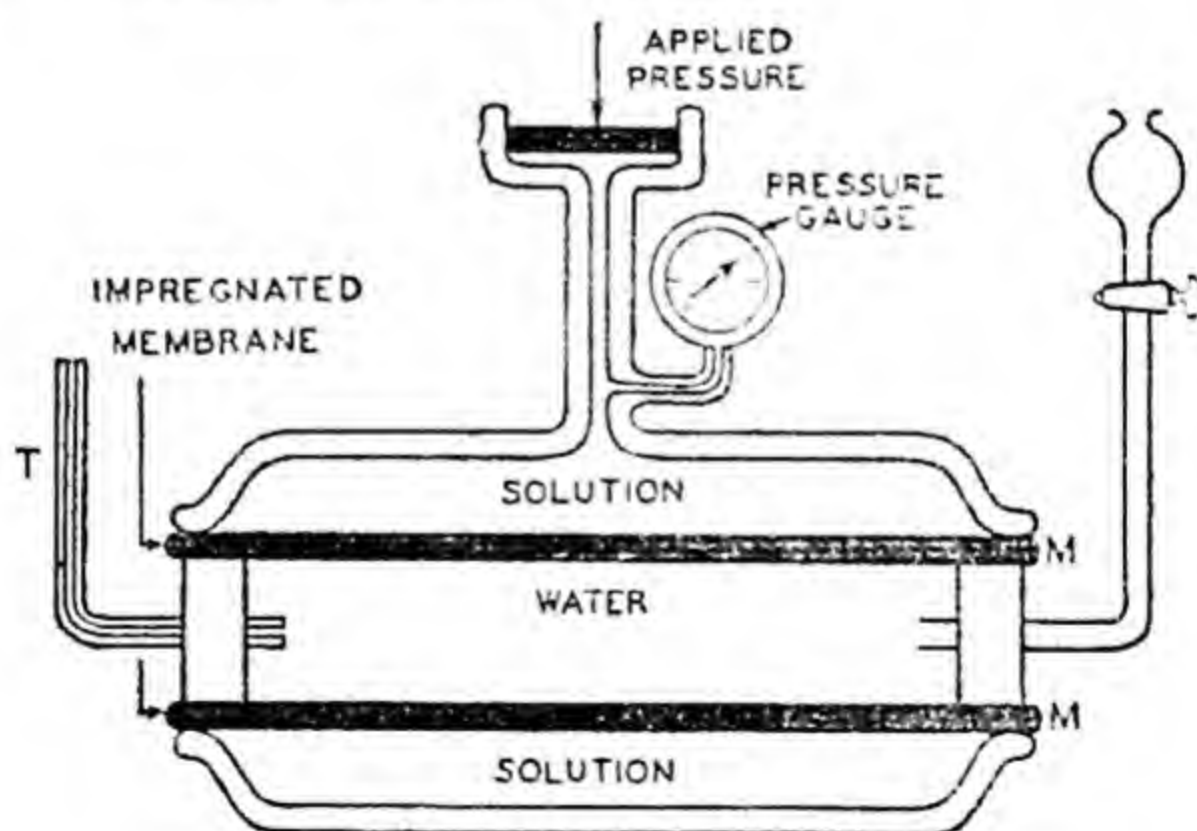

Fig. 66—Measurement of Osmotic Pressure : Apparatus of Berkeley and Hartley.

The apparatus (Fig. 66) consists of two concentric tubes, the inner one, M M being of fine uniform-textured porcelain in the

pores of which is electrolytically deposited the membrane of copper ferrocyanide. The ends of the tube are connected to a fine capillary at one end and a funnel provided with a stopcock at the other. The outer tube made of gun-metal is solidly fixed to the porcelain tube and is provided with an arrangement for applying definite pressures by means of a piston. In the annular space between the two tubes is introduced the solution while the inner porcelain tube contains water up to a definite level in the capillary tube, T. Water from inside diffuses into the solution and the level of water falls in the capillary tube, T. By applying a suitable pressure on the solution, the water in the capillary tube is forced to the original level, and this pressure is the osmotic pressure of the solution. The advantages of the method are that it is very simple and *rapid*, and can record very high pressures, and that the concentration of the solution is not changed by dilution with the solvent.

Determination of Relative Osmotic Pressure –There are some simple methods which may roughly measure and compare the osmotic pressure of solutions. De Vries (1889) employed plant cells for this purpose. These cells are bounded by more or less firm cellulosic walls which are lined with a membrane permeable to water but impermeable to substances dissolved in the cell-sap, *e.g.* glucose, K-salts, etc. If such a cell is immersed in a solution of lower concentration and consequently of lower osmotic pressure than that of the solution inside the cells, no appreciable change in the size of the cell will be observed, since the rigidity of the wall will not allow the water from outside to come in. If, however, the cell is immersed in a solution whose osmotic pressure is greater than that of the cell-sap, there will be a diffusion of water from the interior of the cell to the surrounding solution. This will result in a partial collapse of the cell membrane and would appear under the microscope as shown in the figure (Fig. 65); this phenomenon is known as *plasmolysis*. The retreat of the cell wall can be easily followed with the microscope after staining the cell with a suitable staining dye, *e.g.* indigo carmine, etc.

Fig. 65—Plasmolysis

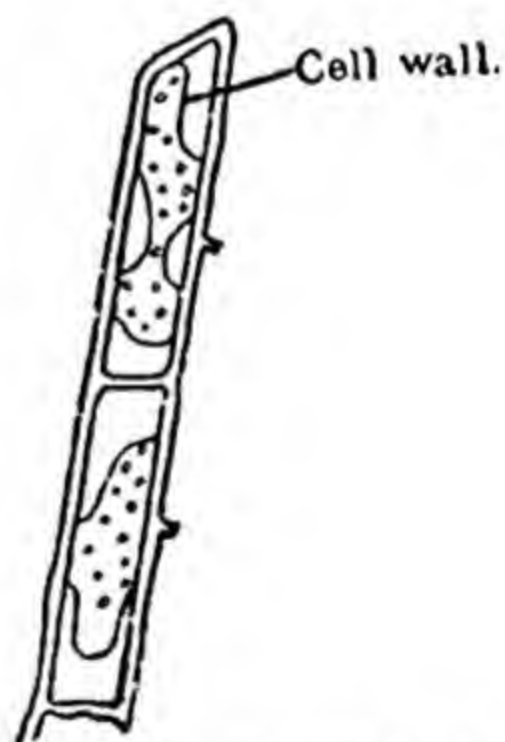De Vries applied this fact to the determination of relative osmotic pressure, by placing plant cells in two solutions to be compared and noticing how much each had to be diluted in order to make solutions which were just able to cause the cell wall shrink. These solutions had the same osmotic pressure and he called *such solutions which have equal osmotic pressure* 'isotonic' or **isosmotic**'.

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Red blood corpuscles may be used in place of plant cells, for, when placed in a strong solution they shrivel, while in weak solutions they swell and burst (*Haemolysis*). A 0·84 per cent sodium chloride solution is isotonic with the contents of the red blood cells and this strength of common salt solution is known in surgery as a '*normal saline*' solution.

Applications of Osmosis—Osmosis plays an essential role in the process of life as it is the principal factor which regulates the flow of water between living cells and their environments. So, it is of great importance in biology, medicine and related sciences. Thus, in medicine, solutions isotonic with blood plasma are used for injection. If pure water is injected in sufficient quantity, it may owing to osmosis pass into the tissues and also cause haemolysis of blood, which may lead to fatal results.

The Nature of Semipermeable Membranes.—Several theories have been advanced to explain the mechanism of semipermeability. Traube believed that the semipermeability was something like sieve action, the pores of the membranes being sufficiently large to allow the water molecules to pass, but small enough to retain the larger solute molecules. The theory is ruled out by the fact that cases of semipermeability are known where the solute molecules are smaller than the solvent molecules. Other theories, which assume the preferential solubility of the solvent in the membrane material or the formation of a loose chemical compound with it, or the adsorption of the solvent on the walls of the bundle of capillaries constituting the membrane, have been advanced, but there seems to be little decisive evidence in favour of any; the solubility theory, however, is more in favour at present.

The thermodynamic interpretation is, however, very clear. A solution has a lower vapour pressure than that of the solvent and so, the vapour distils through the capillaries of the semipermeable membrane from the high vapour pressure (solvent) to the low vapour pressure (solution) side. Since application of pressure is known to increase the vapour pressure of any liquid, osmotic pressure is just equal to the applied pressure, which equalises the vapour pressure of the solvent and the solution, and this pressure would be registered in any osmotic pressure determination by whatever mechanism the membranes might act.

But, whatever may be the correct theory of osmotic pressure and semipermeability, it should be clearly grasped that the membranes are only indices which manifest the existence of osmotic pressure, but the latter is an inherent property of the solution whether the membrane is present or not. Moreover, it may be pointed out that though from kinetic standpoint the osmotic pressure is also equal to the *partial internal pressure* of solute molecules, it is not developed on the surface of a solution, where it is balanced by the forces arising out of surface tension. Solutions of ordinary concentrations may have osmotic pressure equal to several hundred atmospheres, still they can be safely stocked in ordinary glass bottles without the least strain or injury to them.

The Perfect Semipermeable Membrane—It has already been pointed out that no semipermeable membrane is perfect. In other words, there is some leakage of solute through the semipermeable membrane of all types so far prepared. It should be realised that a semipermeable membrane may not have to be a solid. Thus, a layer of liquid or even a gas can as well serve as a semipermeable membrane. In fact, the closest approach to the perfect semipermeable membrane is air or any gaseous phase because if we

keep a solution and a solvent in a closed space, the solvent can pass through the gaseous phase from the solution to the solvent, whereas the solute cannot (see experiment on lowering of vapour pressure Page 188).

It is as much logical to view the empty space as a semipermeable membrane in the above experiment as to regard the fish bladder in Abbe Nollet's experiment or copper ferrocyanide membrane in Pfeiffer experiments as a semipermeable membrane. In fact lately, short air space in between a solution and a solvent has successfully been used as a perfect semipermeable membrane in osmotic pressure measurements.

Van't Hoff's Equation of Osmotic Pressure and his Theory of Dilute Solution —Pteiffer and others had experimentally collected a large amount of data on osmotic pressures, but neither was their significance grasped nor was any regularity recognised by them. We are indebted to the genius of Van't Hoff (1886), for the recognition of a system and regularity in this region, leading to his wellknown theory of solution. Van't Hoff showed that all facts regarding osmotic pressure of dilute solutions of non-electrolytes are embraced by the following equation.

$$P = c\mathbf{RT} \qquad \qquad \dots \text{ (1)-XII}$$

where P is the osmotic pressure, c is the molar concentration (gm. mol per litre), R is the universal gas constant and T is the absolute temperature. This equation is identical with the ideal-gas equation, (P. 7), $PV = RT$. So, we may conclude that the gas equation $PV = RT$ is also valid for substances in dilute solution, where P is the osmotic pressure. Thus complete identity of behaviour of substances in the gaseous state and in solution is established.

This conclusion first reached by Van't Hoff, led him to state: *"The osmotic pressure exerted by any substance in solution is the same as it would exert if present as a gas in the same volume as that occupied by the solution, provided that the solution is so dilute that the volume occupied by the solute is negligible in comparison with that occupied by the solvent."* In an elementary presentation Van't Hoff's equation is very often expressed piecemeal in the form of three different laws as given below.

LAWS OF OSMOTIC PRESSURE

Law 1. *Temperature remaining constant, the osmotic pressure of a solution is proportional to its concentration ($P \propto c$; the symbol $\propto$ stands for 'varies as').*

Since $c = 1/V$, we have $P \propto c \propto 1/V$ or $PV = \text{const}$, where P is the osmotic pressure and V, the volume containing 1 mol of the solute. So, osmotic pressure obeys a law analogous to gas pressure. The following table compiled from the data of

Berkeley and Hartley on sugar solution, illustrates the point. It

Fig. 66—J. H. Van't Hoff (1852—1911) and W. Ostwald (1854—1922)

should be noted that PV is not only fairly constant but has the ideal-gas value in conformity with van't Hoff equation.

Osmotic Pressure and Concentration (T = 0°C)

Moles/litre c	Volume containing one mol, V litres	Osmotic Pressure, P (atmosphere)	P/c	PV
0·02922	34·223	0·655	22·416	22·416
0·05843	17·114	1·310	22·420	22·419
0·0970	10·309	2·18	22·474	22·474
0·1315	7·604	2·95	22·433	22·432
0·2739	3·650	6·14	22·417	22·417

Law 2. *Concentration remaining constant, the osmotic pressure of a solution varies directly as the absolute temperature* $(P \propto T)$.

It is remarkable that the effect of temperature on the osmotic pressure is also similar to the effect of temperature on the pressure of a gas (Charles' law). The following table taken from the work of Morse and Frazer on sugar solution illustrates the validity of the law.

OSMOTIC PRESSURE AND TEMPERATURE

$c = 32.6\ gms/litre$ = 0.1 molal	Temp., °C						
	0°	5°	10°	15°	20°	40°	60°
Osmotic Pressure, P (atmospheres)	2·43	2·45	2·50	2·54	2·59	2·56	2·72
$\frac{P}{T} \times 100$	8·90	8·81	8·83	8·82	8·84		

Law 3. *Equimolecular quantities of different solutes dissolved in the same volume of a solvent exert equal osmotic pressure under identical conditions of temperature.*

Since, equimolecular quantities contain an equal number of molecules, this law is the same as Avogadro's law for gases and may be stated similar to Avogadro's law: Equal volumes of all solutions (non-electrolytes) having the same temperature and osmotic pressure contain an equal number of solute molecules.

Conversely, this means that *every molecule of the dissolved solute, big or small, exerts the same osmotic pressure at the same temperature.* Thus, one giant molecule of say, a protein of a few hundred thousand molecular weight has the same osmotic pressure as a tiny molecule of say, urea. As another illustration, an one per cent solution of glucose has almost double the osmotic pressure of an one per cent solution of cane sugar, because one gram of glucose contains almost double the number of molecules as contained in the same weight of cane sugar. The student should try to clearly appreciate the above point as this is the basic picture of the whole range of colligative properties of solutions.

Deviations from van't Hoff's Equation —These laws of osmotic pressure embodied in the van't Hoff equation, $P = cRT$, are only valid for *dilute* solutions of *non-electrolytes* and marked deviations may occur from either of the three causes:

(i) *High concentration of solute*
(ii) *Association in solution*
(iii) *Dissociation in solution.*

The actual deviation from the osmotic pressure equation due to high concentration of the solute is, for solutes like sugar in water, in the direction of higher values than those given by van't Hoff's equation. This is demonstrated in the following table compiled from the data of Frazer and Myrick (1916) for cane sugar solution at 30°C. Such departure from ideal behaviour was formerly regarded as due to the combination of the solvent and the solute (hydration) and also to molecular association of

Molal concen- tration	Observed Osmotic pressure (atmospheres)	Calculated osmotic pressure	Per cent deviation
0·10	2·47	2·47	0
1·00	27·22	24·72	9
2·00	58·37	49·40	15
3·00	95·16	74·20	23
4·00	138·96	98·90	28
5·00	187·3	123.60	36
6·00	232·8	148·30	56

the solvent. This view no longer finds favour among contemporary physical chemists and active researches are in progress to find out the real cause. We shall discuss towards the close of the next chapter under the heading 'abnormality in solution' about the last two factors mentioned above.

Determination of Molecular Weight from Osmotic Pressure Measurements—The equation, $PV = (g/M)RT$ can be profitably employed for the determination of molecular weight. All quantities are here directly measurable except the molecular weight, M and so M can be calculated out. This method though theoretically sound is not frequently used for the determination of molecular weight due to the great experimental difficulties attending on the measurement of osmotic pressure. However, for high molecular substances such as proteins, polymers, etc. this method is very suitable and is extensively used nowadays. For example, the molecular weight of hæmoglobin was first determined by osmotic pressure method and was found to be 68,000, the same value being obtained from the blood of different animal species. Some numerical examples are worked out to make the method of calculation clear.

Numerical Calculations. The equations to be used are :—

(i) $P = cRT$, (ii) $PV = nRT$ and (iii) $PV = (g/M).RT$

The first equation is useful when concentration is directly expressed in mols per litre : the second one is to be used when the dissolved amount is given in mols only ; and the third equation is suitable if the amount of solute is expressed in grams, or for the calculation of molecular weight.

Example 1. *A solution containing 1 gm. of urea per litre is found to exert an osmotic pressure equal to 304 m.m. at 15°C. Calculate the molecular weight of urea.*

Using the equation, $PV = \dfrac{g}{M}RT$, where $P = \dfrac{304}{760}$ atmos., V = 1 litre

$$g = 1 \text{ gm. and } T = 288° \text{ Abs.,}$$

we have, $\dfrac{304}{760} \times 1 = \dfrac{1}{M} \times 0·082 \times 288$ or M = 59·1.

Example 2. *Calculate the osmotic pressure of a decinormal (N/10) solution of cane sugar at 0°C.*

Using the equation $P = cRT$, where $c = 0.1$ and $T = 273°$ Abs. we have

$P = .1 \times .0821 \times 273 = 2.24$ atmos $= 2.24 \times 76$ cm. of mercury.

Example 3. *A solution containing 10.2 gms. of glycerine per litre is found to be isotonic with a 2 per cent. solution of glucose. Calculate the molecular weight of glycerine (mol. wt. of glucose — 180).*

Using the equation $PV = (g/M) RT$, we have, for the glycerine solution,

$P_1 = (10.2/M) \times RT$ and for the glucose solution, $P_2 \times .1 = (2/180) \times RT$. Since the two solutions are isotonic, $P_1 = P_2$

or $\dfrac{10.2}{M} \times RT = \dfrac{2}{180 \times .1} \times RT$ or $M = 91.8$.

Example 4. *A 0.2 per cent of solution of cellulose acetate in acetone (sp. gr. —0.8) shows an osmotic rise of 23.1 m.m. against pure acetone at 27°C. Calculate the molecular weight of the cellulose acetate.*

Osmotic pressure = 23.1 m.m. of acetone

$= 2.31 \times 0.80 / 13.6$ cm. of Hg.

$= 0.136 = 0.136/76$ atmos.

∴ Applying the familiar equation $PV = (g/M)RT$, we have

$M = \dfrac{gRT}{PV} = \dfrac{0.2 \times 0.082 \times 300}{(0.136/76) \times 0.1} = 27,500$

EXERCISES

Osmotic Pressure.

1. Explain what is meant by (a) Osmosis; (b) osmotic pressure; (c) isotonic solutions; (d) plasmolysis and (e) Semipermeable membrane.

2. Describe an experimental method for the determination of osmotic pressure of solutions, and show how may this be used to determine the molecular weight of a substance? State the limitations of the method.

3. Define osmotic pressure and give reasons which led van't Hoff to establish the analogy between dilute solution and gases. What are isotonic solutions?

4. Name the different methods employed for the determination of molecular weight of a substance. Discuss the relative usefulness and describe the method you would employ for determining the molecular weight of a non-volatile non-electrolyte.

Which of these methods would you employ for determining the molecular weight of (a) cane sugar and (b) acetone?

5. State the laws of osmotic pressure. The osmotic pressure of a 2 per cent. solution of acetone in water is 590 cm. of mercury at 10°C. What is the molecular weight of acetone? [59.8]

The osmotic pressure of a solution of 0.184 gm. of urea in 100 c.c. of water was 56 cm. of mercury at 30°C. Calculate the mol. wt. of urea. [62.1]

A solution containing 3.12 gm. of a substance per litre gives an osmotic pressure of 1.27 atmospheres at 25°C. Calculate the molecular weight of the substance. [60.1]

6. Calculate the gas constant R in litre atmosphere from the observation that a solution containing 34.2 gms. of cane sugar in 1 litre of water has an osmotic pressure of 2.522 atmosphere at 20°C. [0.086]

7. At 10°C, the osmotic pressure of an aqueous solution of urea is 500 mm. of mercury. The solution is diluted and the temperature is raised to 26·8°C, when the osmotic pressure is found to be 105·3 mm. Determine the extent of dilution. [1 : 5]

8. At 24°C, the osmotic pressure of a cane sugar solution is 25·1 atmospheres. What is the concentration of the solution in mols. per litre? [1·029 mol./litre]

9. Calculate the osmotic pressure of a 5 per cent cane sugar solution (mol. wt. −342) and a 5 per cent grape sugar solution at 27°C. What strength of urea (mol. wt. −60) solution is isotonic with this solution? [6·834; 3·596 atm. : 0·877%]

10. 0·1 gm. of a volatile liquid occupies a volume of 4 litres when vaporised at 100°C and 700 m.m. pressure. What would be the osmotic pressure of a 2 per cent solution of this substance? [736·8 cm.]

11. What is the osmotic pressure of human blood as it is known to be isotonic with 0·9 per cent common salt solution? Assume common salt to have an osmotic pressure twice the theoretical value. [7·82 atmos.]

12. A one per cent solution of albumen gives as osmotic pressure of 3·71 cm of water at 27°C. Calculate the molecular weight. [68,500]

13. A solution of alcohol in water has an osmotic pressure of, say, 5 atmospheres. Is this osmotic pressure due to the alcohol or to the water? Has this solution two different osmotic pressures, one due to the alcohol and another due to the water? Discuss fully.

14. Suppose we have two samples of glucose, one, the ordinary glucose and another, the C^{14}—glucose (i.e. all carbon atoms are constituted of the C^{14} isotope of carbon). Will both the samples give the same osmotic pressure for a one per cent solution at 0°C? Discuss quantitatively. [about 7% higher P for ordinary glucose.]

15. A molten magnesium silver alloy containing 10% by wt. of silver, starts solidification when allowed to cool at 630°C with separation of pure magnesium, which latter in the pure state melts at 649°C. Calculate the heat of fusion of magnesium. [2240 cals.]

16. A freezing solution of sugar contains solid ice in equilibrium with a definite concentration of sugar solution. A saturated solution of sugar contains solid sugar in equilibrium with a definite concentrations of sugar solution. In view of the above formal similarity are we justified to call the former solution, a saturated solution of ice in sugar?

17. On venturing out in a car in a snowy region, what should be a better choice to be added to the water in the car radiator as an antifreeze on an equal weight basis, alcohol, glycol or glycerine. Discuss fully giving reasons for the choice.

18. What differences would there be if the same B.P. elevation experiment is conducted in Delhi and on the top of Mt. Everest.

19. Heavy water boils at 101·42° and its molar elevation of boiling point is ten per cent higher than ordinary water. How does its latent heat compare with that of ordinary water? [91·6%]

20. If a solution and a solvent be kept in a closed space separated by an air gap, the solvent passes to the solution in the form of vapour but not the non-volatile solute. The result of interposing a semipermeable membrane as in osmosis is also exactly the same. Are we justified in calling the 'air gap', a semipermeable membrane, and can we use such an 'air gap' in principle to obtain accurate osmotic pressure values?

CHAPTER XIII

PHYSICAL CHEMISTRY OF DILUTE SOLUTIONS

II. Lowering of Vapour Pressure and Related Properties

LOWERING OF VAPOUR PRESSURE

Raoult's Law for Vapour Pressure Lowering—If any non-volatile substance (*solute*) is dissolved in a liquid (*solvent*) it is found that the solution has a *lower* vapour pressure than the pure solvent at the same temperature. This fact was first observed by Gay Lussac and then by Von Babo (1848) and later investigated by Wülner (1856).

The extensive researches of Raoult (1887) on aqueous and non-aqueous solutions led him to a more exact formulation of the law underlying the phenomenon, and this is known an Raoult's Law, which may be stated as follows:—*The relative lowering of vapour pressure is equal to the mol fraction of the solute.* Relative lowering is defined as the ratio of the lowering of vapour pressure to the vapour pressure of the pure solvent, and mol-fraction (see Ch. X) is defined as the ratio of the number of mols of solute to the total number of mols in solution.

If P_0 is the original vapour pressure of the pure solvent and P, the vapour pressure of the solution, then the lowering of vapour pressure is P_0-P and therefore, the relative lowering of vapour pressure, by definition, is $\frac{P_0-P}{P_0}$. If the solution contains n mols of solute dissolved in N mols of solvent, then the mol-fraction of the solution, by definition, is $\frac{n}{N+n}$.

So, according to Raoult's law,

$$\therefore \quad \frac{P_0-P}{P_0}=\frac{n}{N+n} \qquad \cdots \qquad \cdots \qquad \cdots \qquad (1)\text{-XIII}$$

$$=X_{solute} \qquad \cdots \qquad \cdots \qquad \cdots \qquad (1a)\text{-XIII}$$

where X_{solute} . is the mol-fraction of the solute.

For dilute solutions, n can be neglected in comparison with N. and so Raoult's law takes the form,

$$\frac{P_0-P}{P_0}=\frac{n}{N} \textit{(for very dilute solution)} \qquad \cdots \qquad \cdots \qquad (2)\text{-XIII}$$

This law of Raoult holds true only for *dilute* solutions of *non-electrolytes* and is sometimes held as the criterion of a perfect solution.

Alternative Statement of Raoult's Law.—Equation (1) can be easily modified in the following way. Subtracting both sides of equation (1) from unity, we get on simplification,

$$\frac{P}{P_0} = \frac{N}{n+N} \text{ or } P = P_0 X_0 \quad \dots \quad \dots \quad (3)\text{-XIV}$$

where X_0 is the mol-fraction of the solvent. Thus, Raoult's law can be alternatively stated in a simpler way as follows: *The partial vapour pressure of the solvent over any solution is equal to the vapour pressure of the pure solvent multiplied by the mol-fraction of the solvent.*

Fig. 67—J. M. Raoult (1830—1903)

Some data illustrating the validity of Raoult's law for aqueous mannite solution at 20°C are presented below:

Molality	Pressure P	$P_0 - P$	$(P_0 - P) P_0 \times 10^2$ observed	Calc. eqn. (1)	Calc. eqn. (2)
0.0000	17.51	—	—	—	—
0.0634	0.0307	1.753	1.768	1.771
0.1077	0.013	3.506	3.546	3.558
0.2062	0.022	5.265	5.306	5.332
0.4055	.1536	8.772	8.810	8.888
.6094	.2162	12.347	12.327	12.488
.8122	.702	15.945	15.806	16.060
0.9908	.003	17.631	17.512	17.834

Graphical Representation of Raoult's Law.—It is very simple and easy to grasp the implications of Raoult's law graphically. According to eqn. (2), if P, the partial vapour pressure of the solvent over the solution, is plotted against mol-fraction of the solvent, a straight line is obtained, which passes through the origin and ends on the vapour pressure of the pure solvent, P_0, as shown in Fig. 78, curve A (P. 210). The requirements of Raoult's law to be valid is, therefore, very simple and definite, and is that the vapour pressure of any solution if plotted against the mol-fraction of the solvent should fall on this straight line.

THEORETICAL DEDUCTION OF RAOULT'S LAW.—The equation of Raoult can be easily deduced theoretically by a method first used by Arrhenius. Suppose we have an arrangement as shown in the diagram (Fig. 68), where a tall-tube fitted at the bottom with a semipermeable membrane is filled with a solution and is allowed to stand until equilibrium due to osmotic rise is attained. Let the height of the solution above the water-level outside due to osmotic rise, be h. Let s be the mean density of the vapour and ρ, the density of the solution, which for a dilute solution is practically equal to that of the solvent. Let p be the pressure of the vapour over the solution in the tube and p_0, the pressure of the vapour over the surface of the pure solvent. This difference in the pressure is due to the difference of level h, between the surfaces of the solution and the solvent respectively, and is equal to the weight of a column of vapour of height, h and average density s acting over unit cross-section. So, we have, $p_0 - p = hsg$...(i)
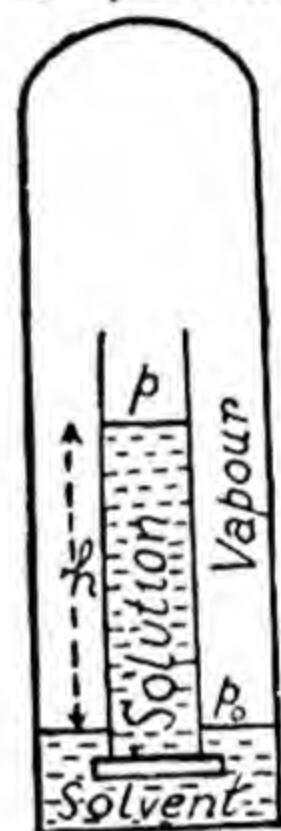

Fig. 68— Deduction of Raoult's Law

But there is another equilibrium co-existing in the system; the weight of the column of liquid inside the tube is balanced by the osmotic pressure, P due to the solution i.e. $P = h\rho g$.........(ii).

Dividing eqn. (i) by eqn. (ii) we have,

$$\frac{p_0 - p}{P} = \frac{s}{\rho}$$

Since the vapour obeys gas law we have

$$p_0 v = \frac{g}{M_0} \cdot RT \text{ or } \frac{p_0 M_0}{RT} = \frac{g}{v} = \frac{mass}{vol. \ c.c.} = s \text{ (density)}$$

Substituting this value of s, we get

$$\frac{p_0 - p}{p_0} = \frac{M_0 P}{\rho RT} \qquad \qquad \qquad \text{(4a)-XIII}$$

i.e. relative lowering of vapour pressure is proportional to the osmotic pressure of the solution and hence, also proportional to concentration.

If n mols of solute are dissolved in V cc. we have according to Van't Hoff's equation

$$P = cRT = (n/V) RT.$$

Putting this value of P in the previous equation,

$$\frac{p_0 - p}{p_0} = \frac{nM_0}{\rho V} = \frac{n}{\rho V/M_0} = \frac{n}{g/M_0} = \frac{n}{N} \qquad \qquad \text{(4b)-XIII}$$

since, $\rho V = $ mass g, and $g/M_0 = $ mols of solvent, N. This is Raoult's equation. Conversely, if Raoult's law (eqn. 1) is assumed, Van't Hoff's equation (eqn. 1-XII) can be easily deduced from eqn. (4a).

Experimental Determination of Lowering of Vapour Pressure.
—Since the lowering of vapour pressure is very small and since
we are interested in the difference, $P_0 - P$, the method has to be
very sensitive and preferably of the differential type, *i.e.*
measuring the difference directly. The methods in more common
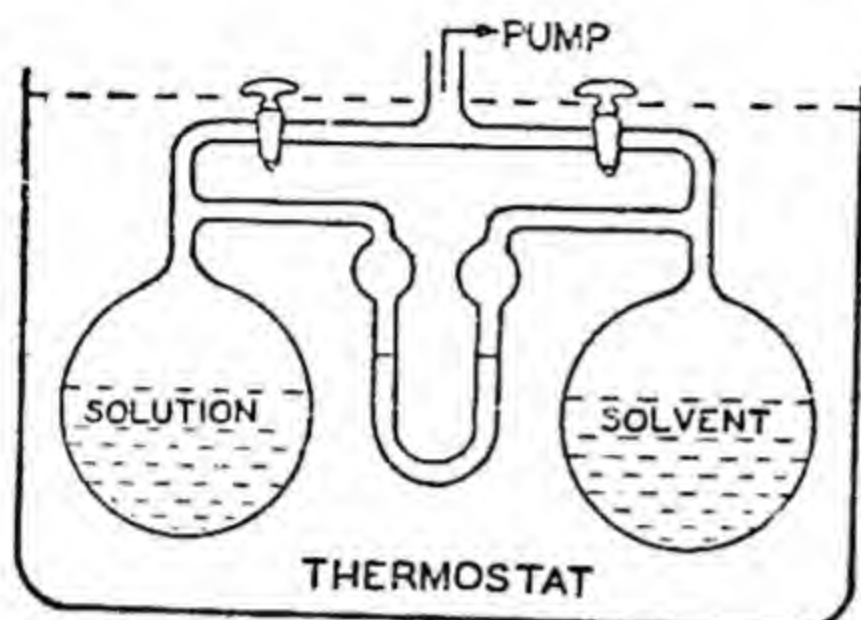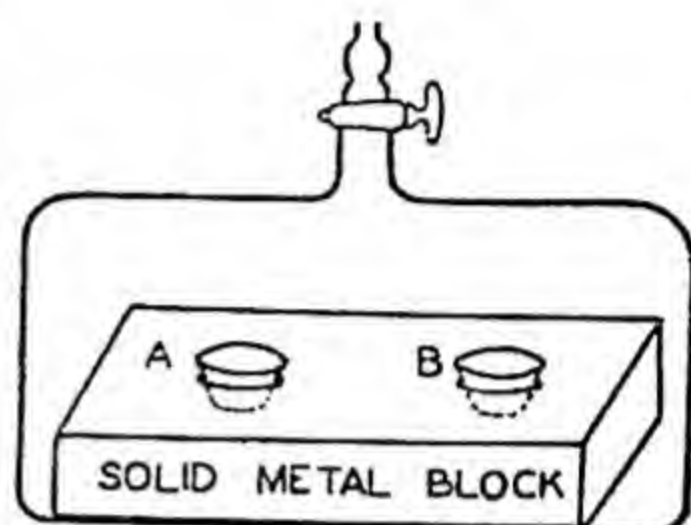use are—

Fig. 69—Tensimeter   Fig. 70—Isopiestic Method

(i) *Differential Tensimeter method,*
(ii) *'Isopiestic' vapour pressure method and*
(iii) *Gas saturation method.*

(i) The tensimeter consists of two bulbs connected by means of a
sensitive oil-filled manometer (Fig. 69). The two bulbs contain the
solution and the solvent respectively. They are connected in common to
a vacuum pump and brisk boiling is allowed to take place to get rid of
the last traces of dissolved gas. The bulbs are now cut off from the pump
and brought in connection through the manometer. The manometer now
reads directly the vapour pressure lowering.

(ii) A recent development in vapour pressure study of solutions is
the extremely ingenious method of Robinson called *isopiestic* vapour
pressure method. The method in principle consists in placing in a closed
space under high vacuum with good thermal contact to prevent temperature
fluctuation, two solutions, one containing a new solute and the other contain-
ing a solute the vapour pressures of whose solutions at various concentrations
are already known (Fig. 70). Vapour from the weaker solution (i.e. higher
vapour pressure) will distil into the stronger solution until the two solu-
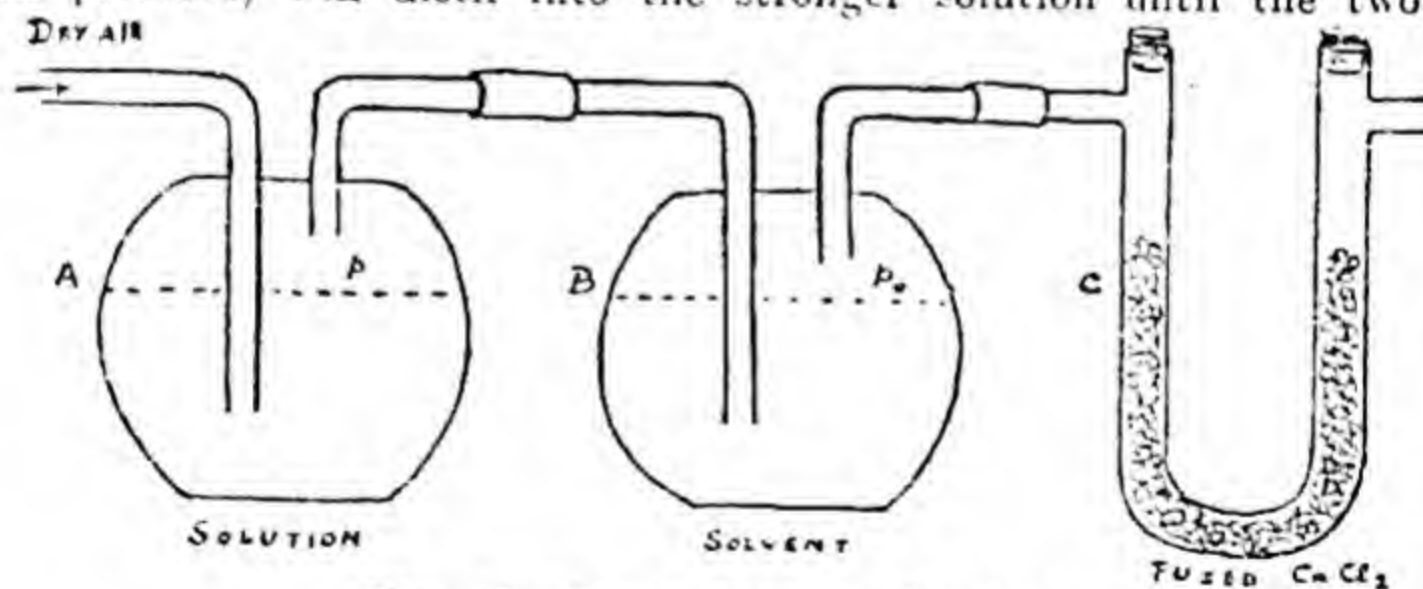

Fig. 71—Gas Saturation Method

tions become of equal vapour pressure *i.e.* of equal molar concentration.
The vapour pressures of the solutions of the new solute in equilibrium with
the former are thus easily obtained.

(iii) The gas saturation method which is a 'dynamic method' in contrast
with the previous two which are 'static methods' is shown in principle
in Fig. 71.

A slow stream of dry air is passed through a series of wash bottles, A (one shown in fig.) containing the solution, the air thus getting saturated up to a pressure p, the saturation pressure of the solution. The wash bottles lose weight which is proportional to the vapour pressure of the solution, p.

This air is now passed through another train of wash bottles, B containing the pure solvent; some of the latter then vaporises to raise the vapour pressure of the air from p to p_0, the saturation pressure of the pure solvent. Therefore, the loss in weight of this system of wash bottles is proportional to $p_0 - p$.

The saturated air now passes through another system of U-tubes, C containing fused $CaCl_2$, to completely absorb the water vapour content of the air. The increase in weight of these drying tubes is proportional to p_0 the saturation vapour pressure of the pure solvent. Therefore

$$\frac{P_0 - P}{P_0} = \frac{\text{Loss in wt. of B}}{\text{Gain in wt. of C}} = \frac{\text{Loss in wt. of B}}{\text{Combined Loss in wt. of A \& B}}$$

So, by measuring the weights of A and B, or of B and C, the relative lowering of vapour pressure can be determined with the help of the above equation.

Molecular Weight from Vapour Pressure Lowering—Let g gms of solute of molecular weight m be dissolved in W gms of solvent of molecular weight, M_0. So, number of mols of solute, $n = g/m$ and number of mols of solvent, $N = W/M_0$. Substituting in the Raoult's law equation for dilute solution, we have,

$$\frac{p_0 - p}{p_0} = \frac{n}{N} = \frac{g/m}{W/M_0} = \frac{gM_0}{Wm.} \qquad \dots \qquad \dots \quad (5)\text{-XIII}$$

So, if the relative lowering of vapour pressure is known for a solution containing a known weight of the solute in a given weight of the solvent, the molecular weight of the solute m can be easily calculated from the above equation. This method of molecular weight determination is of rather limited use due to the experimental difficulty involved in the measurement.

The following table illustrates the molecular weight determination of napthalene (mol. wt. -128) using benzene as the solvent by this method.

Grams Napthalene	Grams Benzene	Mols. Benzene	Vapour pressure in m.m.	Mol. wt.
0·0000	26·53	0·340	639·85	......
0·7913	,,	,,	628·7	131·3
1·3141	,,	,,	621·6	131·7
1·8411	,,	,,	614·5	131·3
2·3446	,,	,,	607·4	129·2
3·3453	,,	,,	594·3	128·5

The student should note carefully from the derivation given in a previous section that M in the above equation is not the molecular weight of the liquid solvent but its molecular weight in the vaporous state in equilibrium with the solution. So, even highly associated solvents like water, acetic acid, etc., might be employed in such determinations since

their vapours are generally only too little associated to affect the result perceptibly.

Example 5. *At 20°C the vapour pressure of ether is 442 mm. of mercury. When 6·1 gms of a substance are dissolved in 50 gms. of ether, the vapour pressure falls to 410 mm. What is the molecular weight of this substance?* (mol. wt. of ether —74).

We have,

$P_0 = 442$ mm.

$P = 410$ mm.

$n = \dfrac{g}{m} = \dfrac{6 \cdot 1}{m}$

$N = \dfrac{W}{M} = \dfrac{50}{74}$

Substituting these values in Raoult's law,

$\dfrac{P_0 - P}{P_0} = \dfrac{n}{N}$ we have

$\dfrac{442 - 410}{442} = \dfrac{6 \cdot 1 \times 74}{m \times 50}$ or $m = 124 \cdot 4$

If the more exact equation, $\dfrac{P_0 - P}{P_0} = \dfrac{N + n}{n}$

is used, we get $m = 115 \cdot 4$.

ELEVATION OF BOILING POINT (*Ebullioscopy*)

Theoretical—Since the vapour pressure of a solution is lower than that of the pure solvent, it follows that a solution will boil at a temperature higher than the boiling point of the pure solvent.
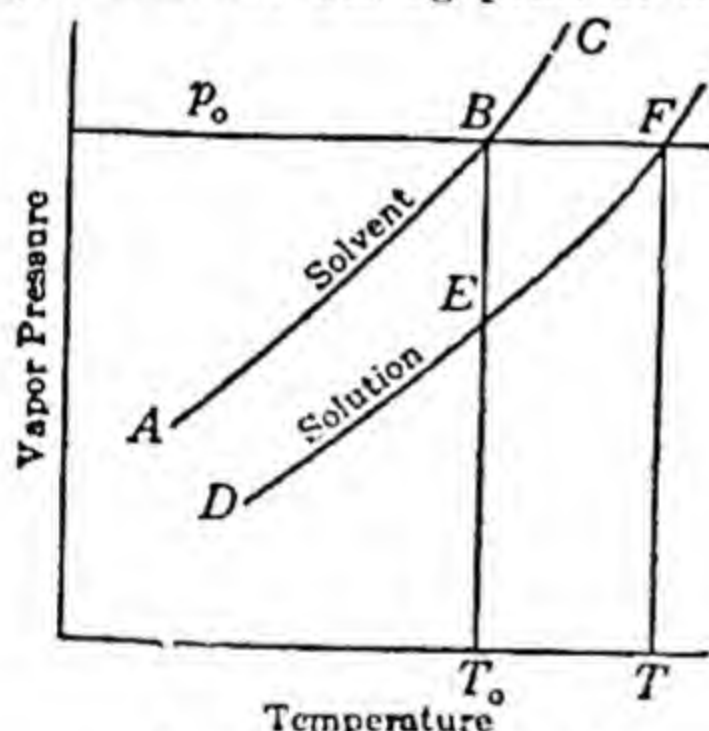

Fig. 72—Principle of B. P. elevation.

This point is more clearly brought forth by the vapour pressure diagram of the solution and the solvent (Fig. 72). The curves AB and DF represent the variation of the vapour pressure of the pure solvent and the solution respectively with temperature; DF runs lower than AB, in accordance with the fact that at any temperature, the vapour pressure of the solution is less than that of the solvent. Now by definition, boiling point is that temperature at which the vapour pressure of a liquid is equal to the external pressure. Let the external pressure be P_0; then from the figure, T_0 and T are the boiling points of the solvent and the solution respectively. It is plainly seen from the figure that T_0 is less than T. So, a solution boils at a temperature higher than that of the pure solvent and this fact can be utilised for the determination of molecular weights of solutes.

Raoult's Law for the Elevation of Boiling Point—The first experimental investigations were made by Blagden (1788) and others, but later researches by Raoult (1871) and Beckmann (1889) have produced a large amount of experimental data which may be embodied in the following two laws generally called Raoult's law.

Law 1. *The elevation of boiling point of a solution is proportional to the concentration (molality) of the dissolved substance. i.e.*

$$\triangle T \propto C_m \text{ or } \triangle T = K_b.C_m \qquad \qquad \text{... (6)-XIII}$$

Law 2. *Equimolecular amounts of different substances dissolved in the same quantity of a particular solvent raise the boiling point to the same extent.*

Like all other laws discussed in this chapter these laws are only valid for dilute solutions of non-electrolytes.

Equation for Boiling Point Elevation— It is now necessary to formulate Raoult's law algebraically. Let us have a solution, where 'a' gms. of solute are dissolved in 'b' gms of solvent, the molecular weight of the solute being M. So, the number of mols of solute is a/M. It is here customary to express the concentration as the number of mols of solute dissolved per 1000 gms of solvent (*molal concentration*). Since a/M mols are present in b gms. of solvent, 1000 gms. of the solvent contain $\frac{a}{M \times b} \times 1000$ moles of solute *i.e.* the concentration, $C_m = \frac{a \times 1000}{b \times M}$.

If the elevation of boiling point be $\triangle T$ we have according to Raoult's law, $\triangle T = K_b . C_m$

$$\therefore \quad \triangle T = K_b \frac{a \times 1000}{b \times M} \qquad \qquad ...\ (7)\text{-}XIII$$

where a = gms of solute, b = gms of solvent, and M = mol. wt. of solute and where K_b is a constant for a given solvent and is called the *molal elevation of boiling point or molecular boiling point constant, or ebullioscopic constant.*

Molecular Boiling Point Constant — The physical significance of K_b is easily derived by putting $c = 1$ (or, $a = M$ and $b = 1000$) in the above equation, when $\triangle T = K_b$. So, *the molal elevation of boiling point, K_b is the increase in boiling point of a solvent, when 1 mol of a solute is dissolved per 1000 gms of the solvent.*

It is of interest to know that K_b can be calculated theoretically from the thermodynamically deduced equation (P. 200),

$$K_b = \frac{0.002T^2}{L} \qquad .. \qquad ... \qquad ... \qquad ...\ (8)\text{-}XIII$$

where T is the boiling point of the solvent on the absolute scale and L, the latent heat of evaporation per gram (*vide* end of this chapter).

MOLAR B. P. ELEVATION (*per 1000 gms. of solvent*).

Solvent	Boiling Point °C	K_b (observed)	K_b (calculated)
Water	100	0·52	0·515
Chloroform	61·2	3·88	3·88
Benzene	80·2	2·57	2·61
Ethyl alcohol	78·3	1·15	1·19

Experimental Determination of Elevation of Boiling Point : Beckmann's Method — The experiment is beset with the following difficulties:—

(*a*) Since the rise in boiling point is very small, the thermometer used should be *sensitive* enough to read a small fraction of a degree.

(*b*) The liquid does not come rapidly in equilibrium

with the vapour and so, there is considerable *superheating* unless sufficient precautions are taken to check it.
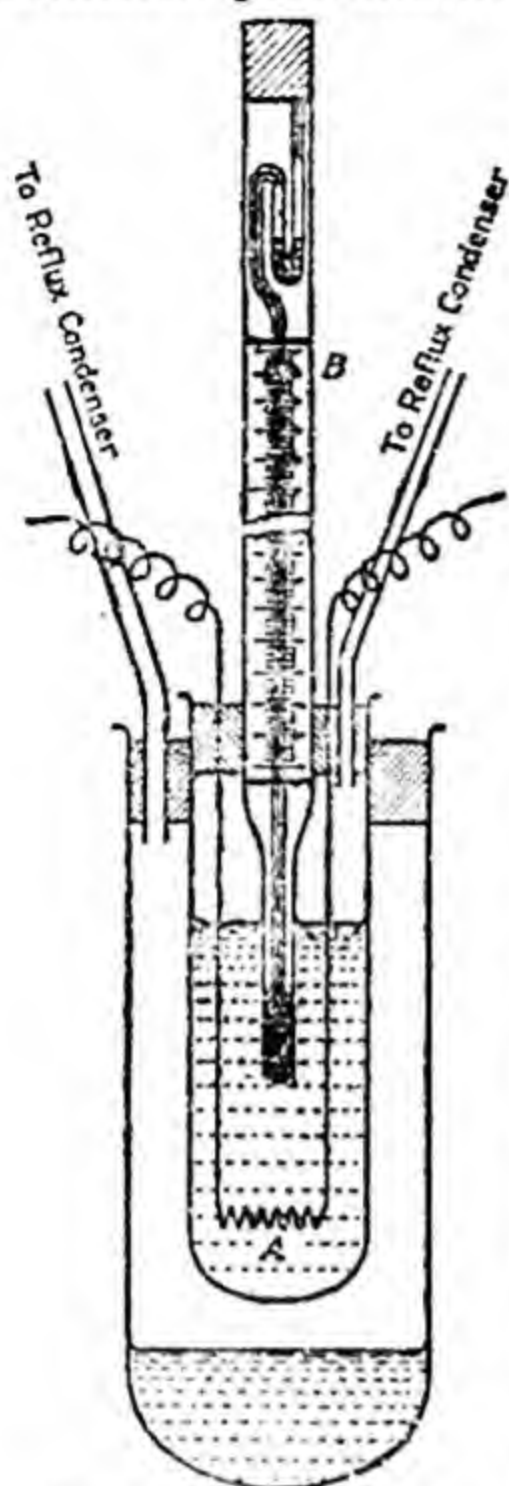
Besides, the chance of superheating is much greater for the solution since to measure its boiling point the thermometer is to be put inside the solution and not in the vapour, though usually the boiling point of any liquid is determined by placing the thermometer in the vapour of the liquid. The vapour coming out from the boiling solution is that of the pure solvent and hence, the temperature recorded on the thermometer if placed in the vapour, would be the condensing temperature of the vapour *i.e.* the boiling point of the pure solvent.

Description of the apparatus—Since the original form of the Beckmann apparatus is practically obsolete, a modern improved form of the same will be described. The main difference with the original apparatus is the employment of electric current instead of gas burners for heating; this is more conveniently controlled and lessens the possibility of superheating. The apparatus is shown diagrammatically in Fig. 73. This simply consists of two test tubes, one inside the other, both fitted with reflux condensers to prevent the escape of vapour. The inner tube, which is the proper boiling tube, is fitted with a Beckmann thermometer and is provided with an electrical heating element, A.

Fig. 73—Beckmann's Apparatus

Experiment—In carrying out an experiment the inner test tube is filled with a measured volume of the pure liquid sufficient to cover the thermometer bulb. A few small beads of platinum or glass are placed in the liquid to facilitate the formation of bubbles. The outer jacket is filled with some of the pure solvent which is kept briskly boiling. A small current is sent through the heating coil, so adjusted as to keep the liquid just smoothly boiling. When everything becomes steady, the thermometer, which is directly graduated to one-hundredth of a degree, is read. The apparatus is allowed to cool slightly, and a weighed quantity of the solute is then introduced through the side tube, and when it has completely dissolved, the boiling point is redetermined by the same method. The difference between the two readings on the thermometer gives the elevation of the boiling point (ΔT). A further quantity of the solute may again be introduced and a second reading may be obtained in the same way.

Cottrell's Apparatus—Beckmann's apparatus and a number of others similarly devised, suffered from serious defects for which boiling point methods could neither yield accurate result nor they became popular. The main defects of all such apparatus are that they cannot overcome superheating satisfactorily and secondly, owing to the increased hydrostatic pressure due to the thermometer bulb being immersed inside the liquid the temperature indicated by the thermometer bulb may be even as much as 0.1°C above the true boiling point at atmospheric pressure.

The ingenious and novel boiling-point apparatus devised by Cottrell is probably the most satisfactory unit for this purpose and since the apparatus was devised and perfected, boiling point method is being increasingly used for molecular weight determination due to its many inherent advantages, viz.—choice of a wider range of solvents, freedom from the messiness of freezing mixture, easier manipulation, higher solubility and ease of solution, etc. One disadvantage, however, is that boiling point is sensitive to slight changes of presure and hence it should be made sure that during the experiment the barometer reading does not change. This method is nowadays extensively used particularly in America.

The apparatus of Cottrell is shown in sketch in Fig. 74. Cottrell places the bulb of the thermometer in the gas phase above the solvent and employs a special 'pumping device', P which continually pumps the liquid up in such a way as to keep the bulb always covered with a thin film of liquid. This 'pumping' device is a creditable development by Cottrell and is simply an inverted funnel branching at the top into three channels which just end on the thermometer bulb. As soon as heating is started with a micro-burner, the liquid goes up through P due to convection and the bubbles of gas formed discharge on the bulb and flows down. The temperature goes up and ultimately remains steady at the boiling point. A weighed amount of solute is introduced through the side tube and the reading repeated, the difference of the two readings giving the elevation of boiling point. The thermometer and the 'pumping' device are surrounded by a tube, S which protects them from coming in contact with the cool liquid flowing down from the condenser.
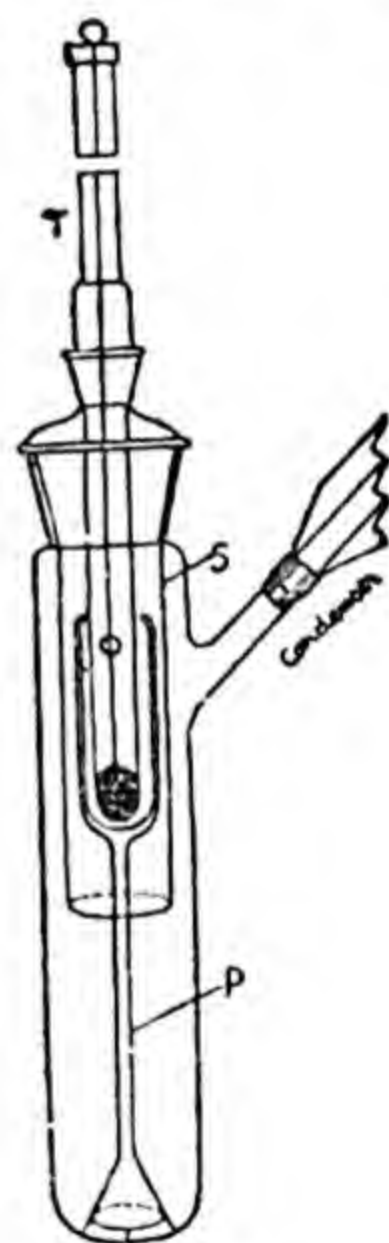
Fig. 74— Cottrell's Apparatus

Beckmann Thermometer — This thermometer was designed by Beckmann for measuring small *difference of temperature* at different points of the temperature scale, and so it is called a *differential thermometer.* The outline of the thermometer is

13

shown in Fig. 75. It consists of a large bulb connected to a very fine capillary tube, with a reservoir of mercury at the top. The long stem of the thermometer is divided into only 5 or 6 degrees and each degree is graduated into 100 divisions. To use this for the determination of boiling point elevation, a quantity of mercury is made to overflow in the reservoir at the top and to be detached from the mercury thread, so that when the thermometer registers the boiling point of the solvent, the mercury column appears somewhere lower down on the scale. This is necessary to keep the mercury column on the scale when measuring the boiling point of the solution and this operation of adjusting the amount of mercury in the thermometer for each liquid is known as *"setting the Beckmann thermometer."*

Molecular Weight from B. P. Elevation—By measuring the boiling point elevation of a solution of known concentration, all quantities in the equation,

$$\triangle T = K_b \frac{a \times 1000}{b \times M} \qquad \dots \qquad (9)\text{-XIII}$$

are known except M, the molecular weight of the solute; so, M can be calculated out. The constant K_b for any liquid is known either by experimenting with a substance of known molecular weight, or can be calculated theoretically as already pointed out.

Numerical Examples :—

Example 6. *Beckmann found that 1·065 gms. of iodine dissolved in 30·14 gms. of ether raised its boiling point by 0·296°C. The molecular elevation constant for ether is 2·11°C. Calculate the molecular weight of iodine.*

Here $\triangle T = 0·296$; $a = 1·065$; $b = 30·14$; $K_b = 2·11$.

Inserting these values in the eqn. $\triangle T = K_b \dfrac{a \times 1000}{b \times M}$

We have, $0·296 = 2·11 \dfrac{1·065 \times 100}{30·14 \times M}$ or, $M = 251$

i.e. mol. wt. of iodine in ether is 251.

Example 7. *A solution containing 0·5042 gms. of a substance dissolved in 42·02 gms. of benzene boils at 80·175°C. Find the molecular weight of the solute, given that benzene boils at 80·0°C and its latent heat of evaporation is 94 cal per gm.*

Here K_b is to be first calculated out.

$$K_b = \frac{·002T^2}{L} = \frac{·002 \times (353)^2}{94} = 2·61.$$

Using the equation $\triangle T = K_b \dfrac{a \times 1000}{b \times M}$

We have, $0·175 = 2·61 \dfrac{·5042 \times 1000}{42·02 \times M}$ or Mol. wt., $M = 179$

Fig. 75—
Beckmann
Thermo-
meter.

DEPRESSION OF FREEZING POINT (*Cryoscopy*)

Theoretical—The fact that a solution has got a vapour pressure lower than that of the pure solvent is sufficient to prove that its freezing point will also be lower than that of the pure solvent. Let us consider the *vapour pressure curve* of the solution and that of the solvent; the latter would run above the former, since the solvent has a higher vapour pressure at the same temperature.

Freezing point of a substance is defined as the temperature at which its solid and the liquid forms can exist side by side; in other words, it is the temperature at which they have the same vapour pressure; if it is not so, the state with higher vapour pressure will completely disappear and will be converted into the state of lower vapour pressure, and an equilibrium between solid and liquid becomes impossible. Therefore, the freezing point may be defined as the temperature at which the vapour pressure curve of the liquid meets the vapour pressure curve of the solid.

Evidently, the point O (fig. 76) is the freezing point of the pure solvent as it is the point where the vapour pressure curve, BO of the solid solvent intersects the vapour pressure curve, OA of the liquid solvent. Similarly, the point, B corresponds to the freezing point of the solution, as it is the point where the vapour pressure curve, DC of the solution meets the vapour pressure curve, OB of the solid solvent. Clearly the temp. T (corresponding to the point, B) is lower than the temp. T_o (corresponding

Fig. 76—Lowering of Freezing Point

to the point, O), proving that the solution freezes at a temperature lower than that of the pure solvent.
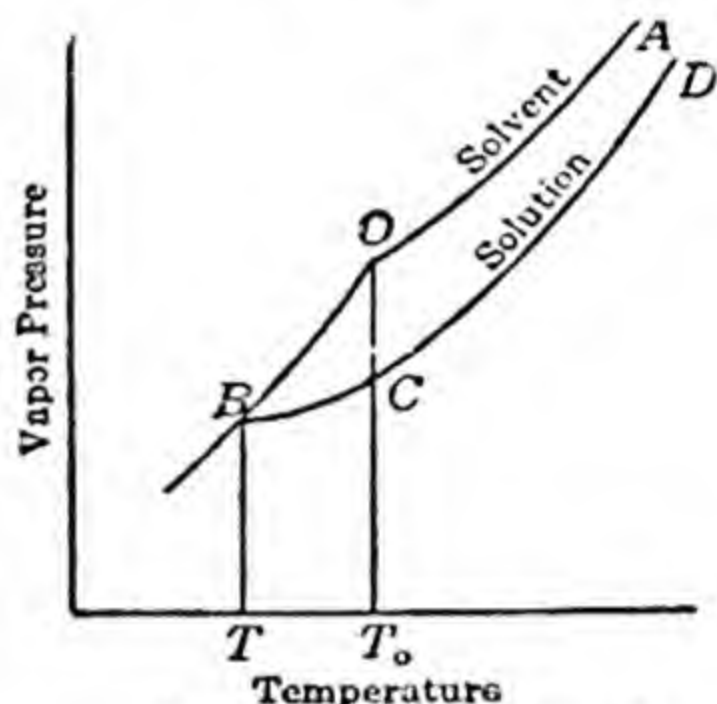
Raoult's Laws on Freezing Point Depression—Blagden (1788) was the first to carry out experiments in this field and he established a rough proportionality between the depression of freezing point and concentration. Raoult (1882-1884) carried out his work with extreme thoroughness and established all the now well-known facts concerning this phenomenon, which may be embodied in the following two laws, which are known a Raoult's law for freezing point depression.

Law 1. *The depression of the freezing point for the same solution is proportional to the concentration of the dissolved substance* $(\triangle T \propto c)$.

Law 2. *Equimolecular quantities of different solutes dissolved in the same quantity of a particular solvent, depress the freezing point to the same extent.*

These laws, are only valid for *dilute* solutions of *nonelectrolytes* and marked deviations may arise due to association, dissociation or high concentration of the solute. Another basic condition for the validity of these cryoscopic laws is that *only the pure solvent will separate during freezing* which will not be

contaminated with the solute as a solid solution. In case the latter happens, there might be even a rise of freezing point instead of a lowering.

Equation for Freezing Point Depression—Since these laws are identically the same as those of the boiling point elevation, the equation is also the same. If the depression of freezing point be $\triangle T$, for a solution of concentration, c_m we have,

$$\triangle T \propto c_m \text{ or, } \triangle T = K_f c_m \qquad \text{... (10a)-XIII}$$

where K_f is a constant called *molar depression of freezing point or cryoscopic constant*. It is customary to express the concentration, c_m in the above equation as the number of moles of solute dissolved in 1000 gms of the solvent (*i.e. molality*). If there are present 'a' gms of solute of molecular weight, M dissolved in 'b' gms of solvent, the number of mols of solute is a/M and so, the number of mols of solute dissolved per 1000 gms of the solvent *i.e.* molal concentration, c_m is $\dfrac{a \times 1000}{b \times M}$. Substituting this value of c_m in the above equation, we have,

$$\triangle T = K_f \frac{a \times 1000}{b \times M} \qquad \text{...} \qquad \text{...} \qquad \text{... (10b)-XIII}$$

where $a=$ gms of solute, $b=$ gms of solvent M = mol. wt. of solute and $K_f =$ molar F. P. constant.

It has been thermodynamically proved (P. 200) that the F.P. constant, K_f for any solvent can be theoretically calculated from the latent heat of fusion per gram, l and the freezing point of the solvent, T (in absolute scale) by the following formula—

$$K_f = \frac{0.002 T^2}{l} \qquad \text{..} \qquad \text{...} \qquad \text{... (11)-XIII}$$

The values of K_f for some of the commoner solvents are given in the following table. It is to be noted that these values are different from the molar elevation of boiling point K_b and usually are of the order of unity (*i.e.* 1 to 10).

MOLAR DEPRESSION OF F. P. (*per 1000 gms. of solvent*)

Solvent	M. P.	K_f (observed)	K_f (calculated)
Water	0°C	1·85	1·86
Benzene	5°	5·12	5·07
Acetic Acid	17°	3·9	3·82
Phenol	40°	5·3	5·05
Formic Acid	8°	2·8	
Camphor	178°	40·0	

Experimental Determination of the Depression of Freezing Point : Beckmann's Method.—A very simple form of apparatus

designed by Beckmann, is widely used for the determination of the freezing point depression, as it affords a considerable degree of accuracy (Fig. 77). It consists essentially of a test tube provided with a side tube for the introduction of the solid and fitted with a rubber cork through which passes a stirrer and a *Beckmann's Thermometer* (for details of the thermometer, see P. 194). The whole is suspended in another large test tube wide enough to provide sufficient air space between them, and the latter in its turn is suspended in a large beaker.

To carry out a determination, the freezing tube is filled with a definite weight of the liquid (solvent), sufficient to dip the thermometer bulb. The outer beaker is filled with a freezing mixture whose temperature is slightly (about 5°C) below the freezing point of the pure solvent. The space between the two test tubes serves as an *air mantle*, preventing direct heat conduction and consequent supercooling. The quantity of mercury in the thermometer is adjusted beforehand so as to get the F. P. of the pure solvent somewhere towards the upper part of the scale (this is called *setting the thermometer*; see P. 194).

Fig. 77—Beckmann's F. P. Apparatus

The temperature gradually falls until the liquid supercools slightly below the true freezing point, when vigorous stirring is made to start solidification. As solidification starts the mercury column shoots up and then remains steady on the thermometer which is read. Now a weighed quantity of the solute in the form of a pill is introduced in the test tube through the side tube and allowed to dissolve in the liquid. The test tube is then placed back in its former position after wiping off any dew which may have deposited. The freezing point of the solution is now determined in the same way, avoiding supercooling as much as possible. The difference in the two readings gives the depression of the freezing point (ΔT).

The freezing point method gives very reliable result, is easy to manipulate experimentally and requires no complicated and costly apparatus. So, it has become the *most widely used of* all methods of determination of molecular weight.

The method has been recently improved upon by Adams and later workers, so much so, that it has become a precision measurement. In principle, the improved method consists in bringing ice in very intimate contact with an aqueous solution

contained in a Dewar flask and in measuring the temperature difference between the mixture and pure ice kept in another Dewar flask, with the help of a thermocouple.

Rast's Camphor Method—Rast (1922) has developed a simple and elegant method of molecular weight determination, which is merely a modification of the freezing point method, such that an ordinary thermometer may be used in place of the very expensive Beckmann thermometer. This has been made possible by the discovery of a number of compounds, whose molar depressions are unusually high (*vide* following Table). The table shows that one mole of any compound dissolved in 1000 gms of camphor, the more usual solvent by this method due to its extensive solvent power, depresses the F. P. by 40°C. Thus, to determine the molecular weight of say, urea by this method, if we make a 2% solution of it in camphor, the depression of F.P. will be 13·3°C, a range easily measurable with accuracy with an ordinary thermometer.

"SOLVENTS" FOR RAST'S METHOD

Solvent	Melting point	Molar Depression
Water	0°C	1·86
Camphor	178°C	40·0
Camphor quinone	199°C	45·7
Borneol	204°C	35·8
Hexachlorethane	187°C	47·7
Camphene	49°C	31·1
Tetrabrommethane	93°C	86·7

All these "solvents" are solids at ordinary temperature and so, it is only necessary to determine separately the melting point of the pure compound (camphor) and that of a mixture of the unknown substance with the compound by the usual capillary method. A mixture containing known weights of the unknown compound and say, camphor as solvent, is melted together to form a homogeneous solution. The mixture is cooled and a small quantity is introduced inside a capillary which is then sealed. The capillary is heated on a sulphuric acid bath and the temperature (read on a thermometer graduated to one-tenth of a degree) at which the solid melts to a clear liquid is noted. Similarly, the melting point of the pure solid (camphor) is determined and by application of the usual equation for F. P. depression the molecular weight is calculated.

This method is advantageous over the other methods in requiring a very small quantity of the substance, but the fundamental conditions of cryoscopy must be fulfilled; the solute should be perfectly soluble in the solvent, and they should not

be isomorphous so that the pure solvent may separate during freezing. If the substance does not dissolve well in camphor, the hydrocarbon camphene or the other solvents shown in the table may sometimes be profitably used.

EXAMPLE 8. *10·4 mg. of a substance added to 0·5 gms of camphor (M. P. : −178°C) melts at 169·7°C ; calculate its molecular weight.*

Here, $\triangle T = 178 - 169·7 = 8·3°C$

$$\therefore \quad M = K \frac{a \times 1000}{b \times \triangle t} = \frac{40 \times 0·0104 \times 1000}{8·3 \times 0·50} = 100$$

Molecular Weight from F. P. Depression—The freezing point depression of a solution is utilised for the calculation of the molecular weight of the solute. If a known weight of the solute is dissolved in a definite quantity of a solvent and the depression of F. P. is measured, then all the quantities in the equation,

$$\triangle T = K_f \frac{a \times 1000}{b \times M} \cdots \qquad \cdots \qquad \cdots \quad (10)\text{-XIII}$$

are known except M, and so the molecular weight M of the solute can be calculated from the above equation. K_f is, of course, known either by experiment with a solute of known molecular weight or from the theoretically deduced equation,

$$K_f = \frac{0·002 T^2}{l} \quad ; \quad \text{where } T = \text{F.P. in absolute scale}$$

and l = latent heat of fusion per gm.

N.B. It should be pointed out that all authors do not follow the same convention as to the values of K_f and K_b. Some define it with reference to 100 gms of solvent, whereas some others define it with relation to 1 gram of the solvent, *i.e.*

$$\triangle T = K \frac{a \times 100}{b \times M} \text{ and } \triangle T = K \frac{a \times 1}{b \times M} \text{ respectively.}$$

Of course, the value of K then becomes respectively 10 times and 1000 times greater than our values, *i.e.* K_f for water becomes 18·5 and 1850 respectively.

F. P. Depression by Isotopes—The question arises what happens to the F.P. (or B.P.) of say, ordinary water if a little 'heavy water', D_2O is added to it. The answer is that there will be no F. P. depression, our foregoing equations being not applicable here. The reason for their non-applicability is that the ice which would now separate would contain the added solute ('heavy water') in the same proportion as in the liquid water with which it is now in equilibrium. In fact, the new water mixture would behave as a pure liquid with respect to almost all physical and chemical properties.

EXAMPLE 6. *A sample of pure prismatic sulphur melted initially at 119·25°C, but in course of a few min. the melting point fell to 114·3°C. When the sulphur had completely melted at this temp. the liquid sulphur was plunged into iced water; 3·6 per cent of the resultant solid sulphur was then found to be insoluble in CS_2. Derive the molecular formula of*

that type of sulphur which is insoluble in CS_2. The latent heat of fusion for sulphur is 9 cals. per gm.

For liquid sulphur, the molar depression, K_f is given by

$$K_f = \frac{\cdot002 T^2}{l} = \frac{\cdot002 \times (392 \cdot 25)^2}{9} = 34 \cdot 18°C$$

Let us call the allotrope of sulphur, which is insoluble in CS_2, S_m In the above experiment this S_m is formed and depresses the freezing point of liquid sulphur.

Given, $a = 3 \cdot 6$; $b = 100 - 3 \cdot 5 = 96 \cdot 4$; $\triangle T = 119 \cdot 25 - 114 \cdot 3 = 4 \cdot 95$.

Inserting in the equation, $\triangle T = K_f \dfrac{a \times 1000}{b \times M}$

we have, $4 \cdot 95 = 34 \cdot 18 \times \dfrac{3 \cdot 6 \times 1000}{96 \cdot 4 \times M}$

or, Mol. wt. of S_m, $M = 258$.

This corresponds to a mol. formula, S_8 (approx.).

Thermodynamic Derivation of the F. P. Depression (or the B. P. elevation) Equation

—The underlying physical concept is very simple and has been already discussed on P. 190 and P. 195 respectively. Taking the case of water, for definiteness, water at $0°C$ has the same vapour pressure as ice at $0°C$, and so the two are in equilibrium at $0°C$. A solution, however, has a vapour pressure lower than that of the solvent at the same temperature and so ice would not at $0°C$ be in equilibrium with a solution. They will have equal vapour pressures at a lower temperature, say, T, where they will now be in equilibrium and this lower temperature is the new F. P.

Let T and T_0, be the F. P. of the solution and the solvent respectively (Fig. 76). The line OB represents the change of vapour pressure of ice with temperature and so assuming OB to be practically linear over this small temperature interval, we can apply Clapeyron equation (P. 140 (20)-X) in the following simplified form.

$$\frac{\triangle P}{\triangle T} = \frac{L}{T_0 (V_2 - V_1)}$$

where $\triangle T$ evidently is the F.P. depression, $T_0 - T$, and V_2 and V_1 are the molar volume of the vapour and the liquid respectively and L is the latent heat of fusion per mol. By rearrangement, we get

$$\therefore \triangle T = \frac{\triangle P}{P_0} \cdot P_0 \frac{T_0 (V_2 - V_1)}{L}$$

Now, $\triangle P / P_0$ is very nearly equal to the relative lowering of vapour pressure and so, according to Raoult's law is equal to X, the mol fraction of the solute. Putting this value of $\triangle P / P_0$ and neglecting V_1 in comparison with V_2, we have

$$\triangle T = X P_0 V_2 \cdot T_0 / L$$

But $P_0 V_2 = RT_0$, and mol fraction, $X = C_m$. $M_0/1000$ for dilute solution, where C_m is the molal concentration, and so we get

$$\Delta T = C_m \frac{RT_0^2}{1000\ L/M_0}$$

Putting $R=2$ cals and $l = L/M_0 =$ latent heat per gram, we have

$$\Delta T = \frac{0.002\ T_0^2}{l}\ .\ C_m$$

which is the same as equations (9) and (11).

A similar argument applies to the case of B. P. elevation except that l would be the latent heat of evaporation and V_1 would be the molar volume of the liquid, which as in the case of F. P. will be negligible in comparison with V_2. So, an exactly similar equation will be obtained.

List of methods for Molecular Weight Determination—So far we have met with various methods for the determination of molecular weight, which are listed below for ready reference :

(1) Vapour Density Method :—(a) *Hofmann's method.* (b) *Dumas' method.* (c) *Regnault's method.* (d) *Victor Meyer's method.*

(2) Osmotic Pressure Method :—

(3) Lowering of Vapour Pressure :—(a) *Tensimeter method.* (b) *Robinson's Isopiestic method.* (c) *Gas saturation method.*

(4) Elevation of Boiling Point :—(a) *Beckmann's apparatus.* (b) *Cottrell's apparatus.*

(5) Lowering of Freezing Point :—(a) *Beckmann's apparatus.* (b) *Rast's method.*

(6) Other Methods :—(a) *Surface tension.* (b) *Steam distillation.* (c) *Specific Viscosity method of Saudinger.* (d) *Ultracentrifuge method of Svedberg, etc.*

Method 1 (d) is extensively used for vapours or easily vaporisable substances and methods 4 (b) and (5) for substances in solution.

ABNORMALITY IN SOLUTION

Ideal and Non-ideal Solutions —It is clear that all the laws of dilute solutions so far discussed would be valid provided the solution obeys Raoult's law. Hence, the validity of Raoult's law is generally held as a criterion of the ideality of a solution.

Now, according to Raoult's law (equation 2) if we plot P, the partial pressure of the solvent against X_0, its mol-fraction, a straight line would be obtained, as shown graphically in Fig. 78, Curve A. Actual solutions however, hardly ever follow Raoult's law over the whole range of concentration. It is generally observed, however, that all solutions tend to obey Raoult's law in very dilute solutions, but the above plot, i.e. P versus X_0. deviates from the ideal curve of Raoult's law at higher concentrations as shown by the typical curves, B and C (Fig. 78). This is the reason why all solutions are said to approach ideality at sufficiently high dilution. Systems which show higher than ideal vapour pressure (Curve B) are said to show *positive deviation,* whereas lower than ideal vapour pressures constitute *negative*

deviation from Raoult's law, and all such solutions are called *non-ideal solutons.*
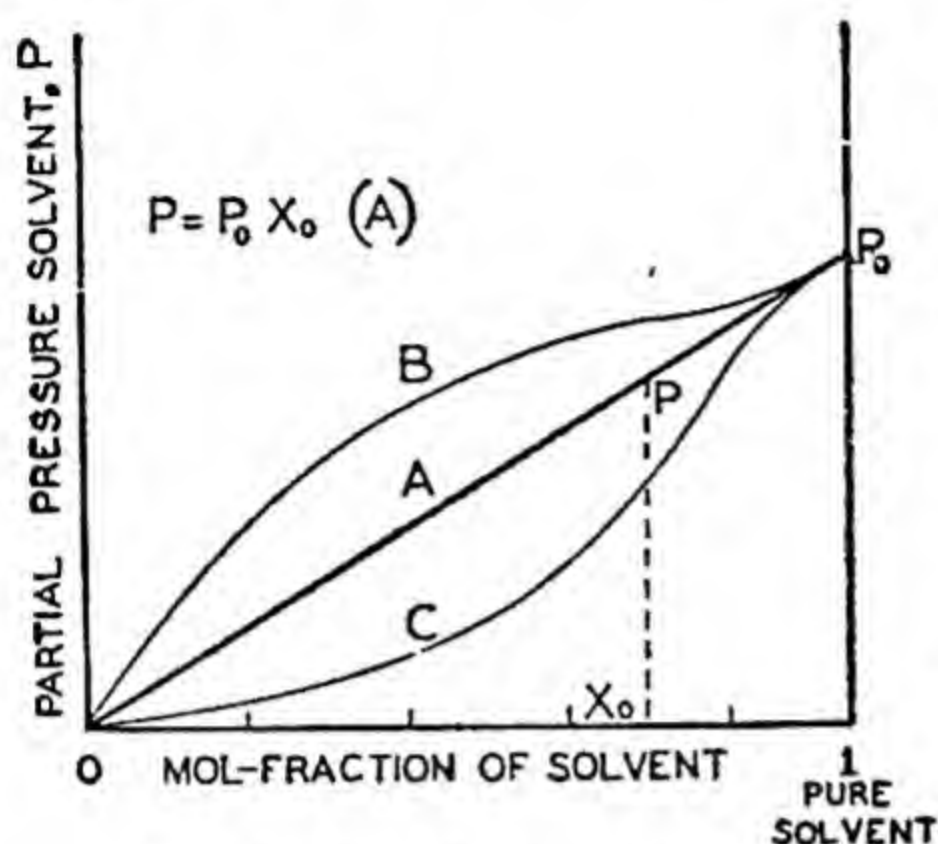

Fig. 78—Raoult's Law and and its Deviations

Evidently, *positive deviation* also implies *lower than theoretical* values for all colligative properties. From a molecular picture, positive deviation is caused when the solvent dislikes the solute and tends to throw it off and so, such deviations are often accompanied by a negative heat of solution (cooling) and expansion on mixing. On the contrary *negative deviation* is caused by strong interaction between the solvent and the solute, and such systems often show positive heat of mixing and contraction on dissolution. In some cases however, the cause of such abnormal behaviour can be traced more definitely, and they are discussed more fully in the following sections.

(*a*) **Association in Solution**—Some systems show strong positive deviation from Raoult's law owing to association in solution. This group comprises substances like acetic acid, phenol, etc., benzene solutions of which show values of osmotic pressure and related properties much lower than what are to be expected from the foregoing equations. Since all the above properties are colligative in nature, *i.e.*, depend on the total number of units in solution these abnormally small values for osmotic pressure, F.P. depression, etc. indicate that the number of particles in solution is much smaller than what is to be anticipated if the solute is broken down into single molecules. So, this type of abnormal values is to be accounted for as due to the association of solute molecules to form aggregates of higher molecular weight.

MOL. WT. OF ACETIC ACID IN BENZENE

Molal Con·. of Acetic acid	Depression of F. P. (°C)	Calculated Mol. Wt.	Degree of Association
0·0033M	0·0155	65·8	1·09
0·0149	0·0539	84·6	1·41
0·0967	0·253	117·0	1·95
0·237	0·608	119·6	1·99
0·509	1·254	114·5	2·07
1·024	2·410	130·2	2·17
1·626	3·644	133·3	2·22

This is evident from the table where it will be found that for acetic acid from deci-normal concentration upwards the calculated molecular weight is about twice its chemical formula (mol. wt.—60) proving that it exists mainly as double molecules in benzene solution.

There is another type of association where the degree of association does not tend to reach a constant value as above but increases with increasing concentration of the solute. This is illustrated in the accompanying table by a rather unusual case of molecular weight determination by the freezing point method of ethyl alcohol dissolved in benzene. We are not sure, however, if such results are due solely to association, or are also contri-buted by positive deviation arising from wide chemical dissimi-larity between the solute and the solvent. Hence, attempt should always be made in cryoscopic experiments to choose a solvent which is as near as possible in chemical nature to the solute to minimise the chance of such deviations.

Mol. Wt. of Ethyl Alcohol in Benzene

Concentration (gm. mol. per litre)	Molecular weight Calculated	Degree of Association
0·10	50	1·09
0·25	62	1·35
0·50	92	1·78
1·00	115	2·50
2·00	162	3·52
3·00	198	4·30

Benzene, carbon tetrachloride, etc. are sometimes called *associating* solvents, whereas water, acetic acid, etc. are called *dissociating* solvents; for, in the former class compounds parti-cularly those containing the hydroxyl and the cyanogen groups are present in the associated state. It is extremely doubtful whether associating solvents do really exert any associating effect, and most probably, associated substances exist in the free condition as complex molecules.

(b) **Dissociation in Solution**—There is another class of substances, viz. the electrolytes, whose osmotic pressures are much greater than what are expected from the equation, $PV = RT$. These solutions also show an abnormally high freezing point depressions, lowering of vapour pressure, etc. Van't Hoff during the earlier period of the advancement of his theory of solution could not satisfactorily account for this anomaly and had to con-tend himself with putting an empirical factor 'i' in the general equation for osmotic pressure. The equation then assumes the form,

$$P_{obs} V = i \, RT \qquad \cdots \qquad \cdots \qquad \cdots \qquad (13)\text{-XIII}$$

where P_{obs}. is the observed osmotic pressure and i, an empirical multiplier introduced by Van't Hoff and so, is called *Van't Hoff's Factor.*

If the theoretical osmotic pressure be P_{theor}., then

$$P_{theor} \cdot V = RT \quad \text{or,} \quad i = \frac{P_{obs \cdot}}{P_{theor \cdot}} \qquad \dots \quad (14)\text{-XIII}$$

i.e. 'i' is the ratio of the actual osmotic pressure to the theoretical osmotic pressure, assuming no dissociation. Since osmotic pressure is proportional to freezing point depression, equation (14) may also be written in the form,

$$\text{Van't Hoff's factor, } i = \frac{(\triangle T'_{obs \cdot}}{(\triangle T'_{theor \cdot}} \qquad \dots \qquad \dots \quad (15)\text{-XIII}$$

and this equation is more in use for determining i because of the comparative ease of experimental determination of $\triangle T$. The values of i for some solutions are given in the following table, where it may be noted that i has a value less than 2 for salts of the type NaCl and less than three for salts like $K_2(SO_4)$.

VALUES OF VAN'T HOFF'S FACTOR 'i'

Concentration	KCl	Mg (SO_4)	$K_2(SO_4)$
0·5	1·80	1·084	2·316
0·1	1·86	1·324	2·459
0·05	1·885	1·420	2·570
0·01	1·943	1·618	2·793
0·005	1·953	1·694	2·857

Arrhenius pointed out that these solutions which exhibit abnormally high osmotic pressure, freezing point depression, etc. are all electrolytes and conduct current in solution. He propounded that a certain fraction of these substances is reversibly broken down into ions in solution, as a result of which the total number of units present in the solution increases. The values of all the colligative properties *e.g.* osmotic pressure, F. P. depression, etc., which are proportional to the total number of units present, therefore, increase in such solutions.

Degree of Dissociation—Arrhenius not only postulated an equilibrium between the ions and the nonionised molecules but also proceeded to calculate the degree of dissociation, α *i.e.* the fraction ionised, of strong electrolytes. His method of calculation was as follows. If one molecule breaks down into two ions we should have $(1-\alpha)+\alpha+\alpha = 1+\alpha$ units in solution from one original unionised molecule. Since osmotic pressure, P, F. P. depression, $\triangle t$. etc., are proportional to the number of units in solution, we have,

$$i = \frac{P_{obs \cdot}}{P_{theor \cdot}} = \frac{\triangle T_{obs \cdot}}{\triangle T_{theor}} = 1+\alpha \qquad \dots \qquad \dots \quad (15)\text{-XIII}$$

where the subscript, *theor.* signifies the corresponding values assuming no dissociation. For the general case of one mol dissociating into *n* ions, we should have

$$i = 1 + (n-1)\alpha \quad \text{or} \quad \alpha = \frac{i-1}{n-1} \quad \cdots \quad \cdots \quad (16)\text{-XIII}$$

which is the general equation for α. Calculations of degree of dissociation of strong electrolytes were freely made with the help of the above equations during the first quarter of the present century, but such calculations are now of historic interest only. We now know that *strong electrolytes are completely dissociated* at all dilutions and no modern chemist would now indulge in such meaningless calculations.

Osmotic Coefficient—The cause of the osmotic properties being less than what it should be assuming complete dissociation is the strong *interionic attraction* between oppositely charged ions. This departure of strong electrolytes from simple theoretical behaviour is expressed nowadays by using a factor, *g*, called osmotic coefficient, which is defined as the ratio of the observed osmotic pressure to the theoretical osmotic pressure assuming complete ionisation of the electrolyte.

$$\therefore \text{ osmotic coefficient, } g = \frac{\text{Van't Hoff's factor, } i}{n}$$

where *n* is the number of ions formed by the dissociation of one molecule of the electrolyte.

Activity coefficient—The most widely used and modern method of quantitatively expressing the departure of strong electrolytes from ideal solution law is the use of activity coefficient. Any ion in solution at a finite concentration behaves, if viewed from ideal solution law, as if it has a concentration different from its actual concentration. In other words its effective concentration is not the same as its actual concentration. The *effective concentration of any ion is called its ion activity.* The activity of an ion varies with the concentration of the ion and is so defined that the activity of any ion becomes equal to the concentration at infinite dilution.

The ratio of the activity of an ion to its actual concentration is called the *activity coefficient* of the ion at the given concentration. For example, a decinormal sodium chloride solution should behave, if there is no interionic attraction, that it is a $N/10$ solution of Na^+ ion as also of Cl^- ion. However, in all its colligative properties it behaves only 80 per cent as effective as it should. So the activity coefficient of the Na^+ and Cl^- ions in this solution is 0·80. Thus, the factor by which the ion concentration is to be multiplied to get the ion activity, *i.e.* effective concentration, is called the *activity coefficient.* For uni-univalent salts *e.g.* KCl, $H(ClO_4)$, etc. the activity coefficients are approximately 0·80 for a $N/10$ solution, 0·90 for a $N/100$ solution, 0·96 for a $N/1000$ solution and approach unity at extreme dilutions. However, the

value of the activity coefficient, γ is not necessarily less than unity and may exceed unity at sufficiently high concentrations.

EXAMPLE 10.—*Calculate the osmotic pressure of a solution at 27°C whose F. P. is −0·326°C.*

Combining equation (3) and (4) we have

$$\frac{P_0-P}{P_0}=\frac{M_0 P}{\rho RT}=\frac{n}{N}\; ;\; \text{But}\; \frac{n}{N}=\frac{a/M}{b/M_0}=\frac{M_0}{1000}\left(\frac{a\times1000}{b\times M}\right)$$

But the braketed expression, according to equation (7) is $\triangle T/k_f$

$$\therefore\; \frac{M_0 P}{\rho RT}=\frac{M_0}{1000}\cdot\frac{\triangle T}{k_f}\; \text{or}\; P=\frac{\triangle T\times\rho RT}{1000\times k_f}\qquad\ldots\quad (17)\text{-XIII}$$

This is the relation between osmotic pressure and F.P. depression (or B.P. elevation). Since ρ is in gms/cc, R in the above expression is in c.c. atmosphere; the equation becomes (R in litre-atmos);

$$P=\frac{\triangle T\rho RT}{k_f}=\frac{0·326\times1\times0·0821\times300}{1·86}=4·32\text{ atmos.}\qquad\ldots\quad (18)\text{-XIII}$$

EXERCISES

Vapour Pressure Lowering

1. Derive the relationship between the osmotic pressure and the lowering of vapour pressure of a solution.

2. How is the vapour pressure of a liquid affected by the presence of a nonvolatile solute? How did the study of this phenomenon led Raoult to correlate the vapour pressure of a solution with the molecular weight of the dissolved substance?

Vapour pressure of ether at 20°C is 442 mm and that of a solution of 6·0 gms of benzoic acid in 50 gms. of ether is 410 mm at the same temperature. Calculate the mol. wt. of benzoic acid in ether. [115·8 ; 124·5]

3. The vapour pressure of benzene (C_6H_6) at 75°C is 639·85 mm. When 2·3·46 gms of napthalene are dissolved in 26·53 gms of the solvent, the resulting vapour pressure is 607·4 mm. Calculate the mol. wt. of napthalene. [129·1 ; *exact equation* :—135·6]

4. The vapour pressure of an aqueous solution of cane sugar (mol. wt.—342) is 756 mm. at 100°C. How many gms of the sugar are present per 1000 gms of water? [100·4 gms.]

5. Pure benzene and CS_2 have vapour pressure of P_1 and P_2 mm respectively at 30°C. Calculate what ratio of weights of napthalene are to be dissolved in equal weights of these solvents each, so that the vapour pressures of the two solutions are equal to a given value, P. How will this ratio change if we use anthracene in place of napthalene? (Assume Raoult's law (dil. soln.) and non-volatility of the solute).

6. What change would be needed in the statement of Raoult's law for an ideal solution when the solvent is non-volatile and the solute is volatile.

7. A 5% by weight of cane sugar solution has a vapour pressure of water equal to 23·69 mm. of mercury at 25°C. Are we justified to express the same fact by saying that the solubility of water in cane sugar under a pressure of 23·69 mm. at 25°C is 95% by weight of water. Discuss fully.

8. Pure and dry nitrogen gas is slowly bubbled through a solution of 2·25 gms. of a non-volatile organic compound in 150 gms. of benzene, and then bubbled through pure benzene. The solution is found to be 2·1540 gms. lighter while the pure benzene suffered a loss in weight of 0·0160 gm. Calculate the molecular weight of the dissolved substance.

[157·7]

F. P. Depression and B. P. Elevation

9. Explain clearly the principle underlying the determination of the molecular weight of a non-volatile solute in aqueous solution by the boiling point method. Describe the apparatus used in this method, and indicate the precautions to be taken to ensure accuracy in measurement.

10. If the vapour pressure of a solution is lower than that of the pure solvent prove that the freezing point and boiling point of such a solution will be respectively lower and higher than that of the pure solvent.

11. A 0.5 per cent. solution of hydrogen peroxide in water freezes at −0.272°C. Determine the formula for hydrogen peroxide. Empirical formula for hydrogen peroxide is HO. Freezing point constant for water = 1.85. [H_2O_2]

12. A solution containing 0.5042 gm. of a non-volatile solute dissolved in 42.02 gms. of benzene boils at 80.38°C. Find the molecular weight of the solute given that the boiling point of benzene is 80.2°C and its latent heat of evaporation is 94 calories per gram. [176.7]

13. A solution of 0.4 gm. of a compound, A in 200 gms. of acetic acid freezes at 16.4°C, the pure acid freezing at 16.5°C; 100 gms. of the same specimen of acetic acid containing 2.23 gms. of another compound, B freezes at 15.6°C. If the vapour density of A is 37 find the molecular weight of B. [91.7]

14. Write notes on Raoult's law. A solution of 0.213 gms. of sodium in 100 gms. mercury lowered the freezing point of mercury by 3.384°C. Determine the number of atoms in a molecule of sodium. (Atomic weight of sodium = 23; F. P. constant of mercury = 42.5). [26.7 ; Na]

15. Give a brief account of the methods that are usually employed, to determine the molecular weight of a substance in solution. 15 gms. of a substance dissolved in 150 gms. of water produced a depression of 1.2°C in the freezing point. Calculate the molecular weight of the substance; K water (100 gms.) is 18.5°C. [154]

16. Explain what is meant by :—(a) Freezing point constant of a solvent. (b) Beckmann's thermometer is a *differential* thermometer.

17. Give an account of Arrhenius' theory of *electrolytic dissociation* and show how it explains the *abnormal* osmotic pressure observed in the case of electrolytes.

18. The F. P. of a blood serum is—0.281°C. Calculate its osmotic pressure in c.m. of mercury at 27°C. k_f = 1.85. [284 *cm*]

19. Give a brief account of the principal methods employed for determining the molecular weight of a substance in solution and discuss their relative merits and limitations.

20. What is meant by degree of *dissociation* of an electrolyte, and how is it determined? What is Van't Hoff's factor?

21. The heat of vaporisation of chloroform is 693 calories and its boiling point is 61°C. 3 gms. of camphor added to 25.2 gms. of chloroform raised the boiling point of the solvent by 0.299°C. Calculate the molar elevation of B. P. of chloroform and also the molecular weight of camphor. [0.32 ; 128.1]

22. The latent heat of fusion of water is 80 cals. and latent heat of evaporation is 536 calories. If the boiling point of an aqueous solution is 100.1°C, what is its freezing point? [0.359°C]

23. The osmotic pressure of a canesugar solution is 5 atmos. at 50°C. Calculate its freezing point supposing the solution to be dilute. Latent heat of fusion of ice is 80 calories. [−.352°C]

[*For more exercises vide* P. 184, *Ex.* 15-20].

CHAPTER XIV

HOMOGENEOUS EQUILIBRIUM

Introduction : "How far" and "How fast" —In connection with any chemical reaction two kinds of information are of vital importance, viz., "how far a reaction would go" and "how fast will it reach the goal". In this chapter we shall study the answer to the first question while the second question which belongs to the province of reaction kinetics will be treated in a later section (Part IV).

In the early days of chemistry chemical union between atoms was ascribed to some kind of vaguely understood forces called chemical affinity, the atoms of stronger affinity being supposed to be able to displace from a compound the atoms of weaker affinity. This idea of chemical affinity or reactivity being solely a property of the atom could not hold long as it came to be slowly realised that not only the chemical nature but also the mass or concentration of a substance has an important influence on the course of a chemical reaction.

Berthollet, the Scientific adviser to Napoleon, in 1799 clearly recognised the fact that the vast deposits of sodium carbonate in Egypt (called 'trona') were formed by the interaction of the common salt present in sea water on the limestone present in the rocks, according to the equation,

$$2NaCl + CaCO_3 = Na_2CO_3 + CaCl_2,$$

though when conducted in the laboratory this reaction goes the reverse way, leading to the precipitation of $CaCO_3$, according to the equation, $CaCl_2 + Na_2CO_3 = 2NaCl + CaCO_3$ (ppt.). Berthollet explained this by saying that the *large mass of sodium chloride present in sea water more than compensates for its weak chemical affinity* and drives the reaction in opposite direction.

Reversibility of Reactions—It became thus gradually appreciated that most reactions are reversible and can proceed both ways, and they reach a position of equilibrium depending on the relative masses of the different constituents and on the external physical conditions. The effect of relative masses of the reactants on the position of equilibrium was first systematically studied by Berthelot and Pean de St. Gilles in 1862 whose results very clearly demonstrated the effect of mass and paved the way for the law which was to come two years later and to be regarded as the greatest and the most fundamental law of physical chemistry. They showed that if one mol of acetic acid is reacted with increasing amounts of alcohol the percentage of acid converted into ester according to the equation,

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$
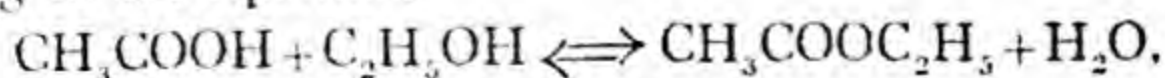
also increases as shown in the following table compiled from their data, thus clearly showing the effect of mass on the course of a chemical reaction.

Equivalents of alcohol	Ester formed (per cent)	Equivalents of alcohol	Ester formed (per cent)
0·2	19·3	2·0	82·8
0·6	42·3	4·0	88·2
1·0	66·5	12·0	93·2
1·5	77·9	50·0	almost 100·0

Law of Mass Action—The credit of first enunciating the law regarding the influence of the relative masses of the reacting substances is usually attributed to two Norwegian chemists. Guldberg and Waage, who in the year 1864 stated the law of mass action as follows—*The rate of any chemical reaction is proportional to the active mass of each of the reacting substances; the active mass in a homogeneous system is defined as the number of gm molecules of the substance present per unit volume i.e. the molar concentration.* This law can be easily deduced from thermodynamic considerations (see later).

Mathematical Formulation of the Law of Mass Action— To apply the law to specific cases it is necessary to formulate the law mathematically. Let us take a simple case of a reversible reaction represented by the equation—

$$A + B \rightleftharpoons C + D$$
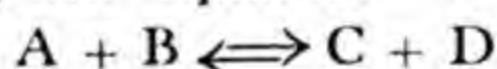
An actual reaction of this type is the esterification of alcohol according to the equation,

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$
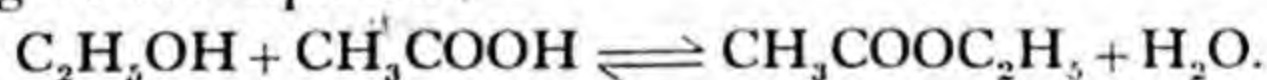
Let us start with A and B only at the beginning without any C and D. The initial speed is proportional to the concentration of A and to the concentration of B and therefore, proportional to the product of their concentrations. As the reaction proceeds the speed of the direct reaction $(A + B \longrightarrow C + D)$ gradually decreases, since the amounts of A and B go on decreasing owing to their gradual conversion into C and D. But as soon as some quantities of C and D accumulate in the system, the back reaction $(C + D \longrightarrow A + B)$ sets in, and as more and more quantities of C and D accumulate in the system the speed of the back reaction gradually increases. So, the speed of the direct reaction decreases, while the speed of the reverse reaction gradually increases, and ultimately *a condition is reached when the speeds of the forward and the backward reactions become equal.* The system has then reached equilibrium and no further change of concentration will take place. Such a condition is called a state of **dynamic equilibrium** or **balanced state.** The condi-

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tion of the system does not apparently change, not because all reactions have stopped, but because *as many molecules decompose in a given time as are formed by the reverse reaction.*

Let [A], [B], [C] and [D] represent the molar concentrations of the substances, A, B, C and D respectively *when equilibrium has been finally reached.*

Then, the speed of the forward or direct reaction

$$\propto [A] \times [B]$$
$$= k_1 \times [A] \times [B]$$

where k_1 is the velocity constant of the direct reaction ; and the speed of the reverse reaction

$$\propto [C] \times [D]$$
$$= k_2 \times [C] \times [D]$$

where k_2 is the velocity constant of the reverse reaction. At equilibrium, speed of the forward reaction=speed of the backward reaction ;

$$\text{or, } k_1[A][B] = k_2[C][D]$$

$$\text{or, } \frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = K \qquad \dots \qquad \dots \quad (1)\text{-XIV}$$

where K is called the **equilibrium constant** or **mass law constant** for the above reaction and is equal to the ratio of the two velocity constants k_1 and k_2. It should be pointed out that K is a constant at a given temperature and its value changes with temperature.

N.B. It is to be noted that [A], [B], etc. are not the initial concentrations, but the concentrations when equilibrium has been *finally* attained and they are to be expressed *in moles per unit volume* and not in grams.

Also, we shall follow the convention of writing the resultants on the numerator and the reactants in the denominator in the expression for K.

If the reaction be of the type $2A \rightleftharpoons C + D$, we may regard it as $A + A \rightleftharpoons C + D$, and the mass law equation becomes

$$K = \frac{[C] \times [D]}{[A] \times [A]} = \frac{[C] \times [D]}{[A]^2} \qquad \dots \qquad \dots \quad (2)\text{-XIV}$$

In the general case if the reaction is represented by

$$aA + bB + \dots \rightleftharpoons gG + hH \dots$$

we have, $$K = \frac{[G]^g \times [H]^h \times \dots}{[A]^a \times [B]^b \times \dots} \qquad \dots \qquad \dots \quad (3)\text{-XIV}$$

where the bracket [ ] represents the concentration of the respective substance present at equilibrium.

This equation is the most generalised mathematical expression for the law of mass action and may be stated as follows :—

At equilibrium the product of the concentrations of the substances formed in a reversible reaction, each raised to a power which is the

co-efficient of its formula in the chemical equation, divided by the product of the concentrations of the reacting substances, each raised to a power which is the co-efficient of its formula in the chemical equation, is constant.

Gaseous Reactions : K_p and K_c—In applying the law of mass action to the case of a gaseous equilibrium, we can also substitute the partial pressures for concentrations in the mass law equation since the concentration of a gas is proportional to its partial pressure. Taking a gaseous reaction represented by $A + B + \rightleftharpoons C + D$ and representing partial pressures by the symbol "P" with proper suffixes,

we may get, (i) $K_p = \dfrac{P_C \times P_D}{P_A \times P_B}$; and (ii) $K_c = \dfrac{[C] \times [D]}{[A] \times [B]}$ ... (4)-XIV

where K_p is the equilibrium constant. This equilibrium constant, K_p is not necessarily the same as the other constant, obtained by using concentration, which is called K_c, but when there is little chance of confusion we shall use the symbol K generally.

The relation between Kp and Kc can be easily deduced. Since according to equation (2)-II, we have $PV = nRT$, and so, $P = (n/V)RT = cRT$ where c is the concentration, *i.e.*, in the present notation $P_A = [A]RT$ and so on.

Substituting this value of P in the definition of K_p for the general reaction, $aA + bB + ... \rightleftharpoons gG + hH + ...$ we get

$$K_p = \frac{P_G{}^g \times P_H{}^h \times ...}{P_A{}^a \times P_B{}^b \times ...} = \frac{[G]^g \times [H]^h \times ...}{[A]^a \times [B]^b \times ...}(RT)^{(g+h+...)-(a+b+......)}$$

$$\therefore \quad K_p = K_c(RT)^{\triangle n} \qquad ... \qquad ... \quad (5)\text{-}XIV$$

where $\triangle n$ is the increase in the number of moles during the reaction.

Example 1. *Kc for the reaction, $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$ at $600°C$ is 61·7. Calculate Kp.*

Here, $\triangle n$ = increase in number of moles = No. of moles of products *minus* No. of moles reactants = $1 - 1\frac{1}{2} = -\frac{1}{2}$. Substituting in equation (5) we get, $Kp = 61·7 \times (0·0821 \times 873)^{-\frac{1}{2}} = 59·8$. Note that the units of conc. and pressure are mols/litre and atmospheres and R is in litre-atmos.

Criteria of Chemical Equilibrium and Reversibility—Chemical equilibrium in general must satisfy the following three criteria.

(a) *Permanancy of Equilibrium.*

(b) *Approachability from both sides.*

(c) *Incompleteness of the reaction.*

(a) PERMANANCY OF EQUILIBRIUM—*A system when it has once reached equilibrium will remain unmodified in composition for ever, if the external conditions are kept-unchanged.* In nature however, some systems are met

with, which are not in true equilibrium but seem to be so, because the change of the system towards equilibrium is so slow as to be beyond detection but a suitable shock or impulse will at once change the system to equilibrium. For example, a mixture of hydrogen and oxygen at room temperature though apparently stable combines in presence of platinised asbestos to produce a state of true equilibrium. Such an *apparent equilibrium* is also called *false equilibrium* or *metastable state*.

(*b*) APPROACHABILITY FROM BOTH SIDES—When an electric spark is sent through pure ammonia, 93% of it gets decomposed into nitrogen and hydrogen. But if an electric spark is sent through a mixture of nitrogen and hydrogen in the ratio 1 : 3, only 7% of the gases combine and 93% of nitrogen and hydrogen is left. Thus it is seen that *whether we start with pure ammonia or with its decomposition products, the same state of equilibrium is finally reached whose composition cannot further be changed.* This fact was first experimentally established by Berthelot and St. Gilles in their classical researches on the esterification of acetic acid with ethyl alcohol and is *the surest criterion of true equilibrium.*

(*c*) INCOMPLETENESS OF CHEMICAL REACTIONS—From the nature of the equation for equilibrium constant, it will be easily seen that none of the substances can vanish. For, then the concentration of one of the substances will be zero, which makes the value of the equilibrium constant K either zero or infinity, and K in that case loses its significance. So, a *reversible reaction will never be complete in any direction if the products are allowed to remain in the system.* Many reactions, *e.g.* combination of hydrogen and chlorine, etc. appear to be complete, but this is due to the equilibrium point lying very close to one side.

Irreversible Reactions—Theoretically, all reactions are reversible. There are however many reactions which could hardly be thought of as reversible. It would be extremely difficult indeed to establish conditions to run in a reverse direction such reactions as $KClO_3$ decomposition, burning in oxygen of carbon and carbon compounds, digestion of food, etc. However, in principle all these and similar reactions are reversible and in fact, it is even possible to calculate equilibrium constants for them from thermodynamic free energy considerations. Our inability to run such reactions in the reverse way is simply a reflection on our inadequate knowledge to produce the right experimental conditions, and we conclude that there is no existence of truly irreversible reactions.

Dissociation—*Reversible decomposition of a single molecular species to form a number of neutral molecules or atoms is called* thermal dissociation. Gaseous dissociation (P. 42) is a special type of thermal dissociation where the reactant molecules and the products happen to be all gaseous. Examples of thermal dissociation are:—$CaCO_3 \rightleftharpoons CaO + CO_2$: $NH_4Cl \rightleftharpoons NH_3 + HCl$: $I_2 \rightleftharpoons I + I$: etc. Thermal dissociation, being truly reversible, has provided many interesting cases of illustration of the law of mass action and we shall closely examine quite a few later on.

Dynamic Nature of Equilibrium—That an equilibrium is not a cessation of all reactions but is due to an equality of speeds for the forward and the backward reactions has been experimentally proved recently by using radioactive isotopes as tracers, an example being cited below.

Arsenious acid is oxidised to arsenic acid by iodine in aqueous solution, the iodine being generally used in presence of an iodide, so that the iodine is present in solution as I_3^- ions. The equilibrium is

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 3I^- + 2H^+$$
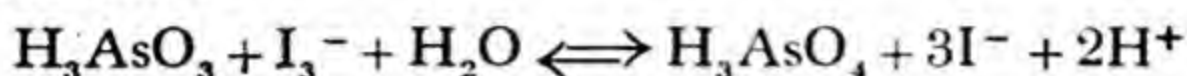
Arsenic by neutron bombardment becomes radioactive arsenic from which radioactive arsenious acid can be prepared by the usual method. In a blank experiment it is observed that this active arsenious acid remains unchanged in solution in presence of inactive (ordinary) arsenic acid. Now if an equilibrium mixture as shown by the above equation is made up using radioactive arsenious acid, the other components being ordinary chemicals, it is observed as expected that the net equilibrium does not shift. However, if the arsenic acid and the arsenious acid present in the equilibrium system, be examined from time to time for their radioactivity, it is found that the former becomes radioactive and the latter loses radioactivity at the same rate, and this rate is exactly equal to the rate expected from the law of mass action. This conclusively proves that even at equilibrium though the net reaction stops, the forward reaction and the backward reaction go on at equal rate.

Application of the Law of Mass Action —It is now proposed to discuss some applications of the law of mass action to homogeneous liquid and gaseous systems to investigate how far the equations derived on the basis of the law of mass action agree with experimental data.

(a) **Esterification of ethyl alcohol** —It is a homogeneous liquid system and the reaction is represented by the equation,

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$
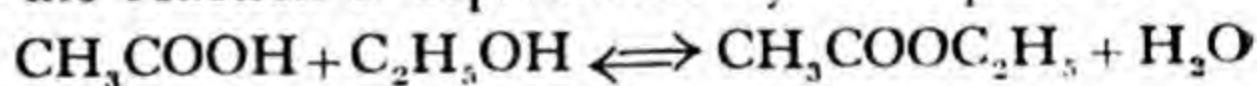
Original :— a b o o

At equilibrium :— $a-x$ $b-x$ x x

The equation for equilibrium is evidently,

$$\frac{[CH_3COOC_2H_5] \, [H_2O]}{[CH_3COOH] \, [C_2H_5OH]} = K \qquad \dots \qquad \dots \text{(6)-XIV}$$

N.B.—We shall throughout adopt the convention of writing the mass law equation with *the resultants (right hand side) in the numerator and the reactants (left hand side) in the denominator* though the opposite convention is used by some authors.

Let us start with 'a' mols of acid and 'b' mols of alcohol and let 'x' mols of the acid and alcohol react to form ester to produce equilibrium. Then the final system will contain $(a-x)$ mols of acid, $(b-x)$ mols of alcohol, x mols of ester and x mols of water. If the total volume be 'v', then the equilibrium concentrations (mols per litre) of acid, alcohol, ester and water are $\dfrac{a-x}{v}$, $\dfrac{b-x}{v}$, $\dfrac{x}{v}$, and $\dfrac{x}{v}$ respectively.

So, substituting in the mass law equation we get,

$$\frac{\dfrac{x}{v} \times \dfrac{x}{v}}{\dfrac{a-x}{v} \times \dfrac{b-x}{v}} = \frac{k_1}{k_2} = K \quad \text{or,} \quad \frac{x^2}{(a-x)(b-x)} = K \quad \dots \quad (7)\text{-XIV}$$

It will be noted that the above equation for equilibrium constant, K does not contain v, and so the position of equilibrium is here independent of the total volume of the system. In fact, in any reaction in which the number of molecules does not change due to the reaction, the position of equilibrium is independent of the total volume of the system.

This reaction was first investigated by Berthelot and Pean de St. Gilles. They took 1 mol of acid with different amounts of alcohol in sealed glass tubes and heated up the reaction mixtures to 100°C for rapid attainment of equilibrium. The tubes were then rapidly cooled and the contents were analysed for the undecomposed acid by acidimetric titration, from which the amounts of ester formed were easily known. Their data were found to agree very closely with the values calculated from the law of mass action as shown in the following table.

Alcohol a	Ester formed (observed)	Ester formed (Calculated)
0·05	0·05	0·049
0·18	0·171	0·171
0·33	0·293	0·301
0·50	0·414	0·423
1·50	0·789	0·785
2·24	0·876	0·864
8·00	0·966	0·970

Method of Application of the Law of Mass Action—In applying the law to specific reactions it should be made clear that the law does not help in any way to find out independently the extent of a chemical reaction from a given amount of the reactants. The law only makes it possible to calculate the equilibrium starting from *any* proportion of the reactants, provided the equilibrium is experimentally determined with a *particular* proportion. In other words, given the information that one mol of acetic acid and one mol of alcohol form only two-third mol of ester, we can calculate with the help of mass law the yield of ester from any other relative proportions of the acid and alcohol as illustrated by the following example.

EXAMPLE 2.—*When alcohol and acetic acid are mixed together in equimolecular proportion 66·5 per cent are converted into ester. Calculate how much ester will be formed if 1 mol acetic acid is treated with 0·5, 4 and 8 moles of alcohol separately.*

For 1 mol. of acid and 1 mol. of alcohol, ·665 moles are converted into ester and water *i.e.* $a=1$, $b=1$, $x=·665$. Substituting in the mass law eqn.

$$K = \frac{[\text{ester}]\,[\text{water}]}{[\text{alcohol}]\,[\text{acid}]} = \frac{x^2}{(a-x)\,(b-x)} = \frac{(·665)^2}{(1-·665)\,(1-·665)} = 4 \text{ (approx.)}$$

For 0·5 mole of alcohol and 1 mole of acid $a=0·5$, $b=1$ and so, we have

$$4 = \frac{x^2}{(·5-x)\,(1-x)}$$

This is a quadratic equation which on solution yields two values, $x=0·423$ and $1·57$, of which the latter value is inadmissible because, 0·5 mol alcohol can never produce 1·57 mols of ester. Hence, number of mols of ester formed $= 0·423$. Similarly, when $a=4$, $b=1$, we have, $x=0·93$ and when $a=8$, $b=1$, $x=0·97$. Therefore, the acid is 42·4, 93 and 97 per cent converted into ester respectively.

(*b*) **Formation of Hydriodic Acid** —This is an example of homogeneous equilibrium. The reaction is

$$\underset{a-x}{H_2} + \underset{b-x}{I_2} \rightleftharpoons \underset{2x}{2HI}$$
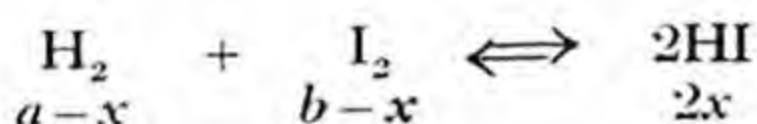
Let '*a*' mols of hydrogen and '*b*' mols of iodine be heated in a vessel of volume, v, and let $2x$ mols of hydriodic acid be formed. Therefore, the number of mols of hydrogen and iodine left at equilibrium are respectively $(a-x)$ and $(b-x)$. Substituting these values in the mass law equation we have

$$K = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{4x^2}{(a-x)\,(b-x)} \quad \cdots \quad \cdots \quad (8)\text{-XIV}$$

Here, again the equilibrium point is independent of the volume or pressure, and K_p and K_c have the same value.

This reaction has been experimentally studied by *Bodenstein* (1899). Known amounts of hydrogen and iodine are heated together in various proportions in sealed tubes to a temperature of 444°C (boiling sulphur). After a time sufficiently long for equilibrium, the tubes are suddenly cooled and the amount of hydrogen left is determined by absorbing the iodine and hydrogen iodide in potassium hydroxide; the liquid obtained by absorption is analysed by the usual methods of chemical analysis. The validity of the law of mass action is demonstrated in the following table compiled from some recent data for this reaction. In the first four experiments reported in the Table the equilibrium was approached from the formation side and the last two from the decomposition side. It would be seen that K remains constant in all the experiments proving conclusively the reversibility of the reaction and the validity of the law of mass action.

Partial Pressure, atm.			K_p
H_2	I_2	HI	
0·1645	0·09783	0·9447	0·01803
0·2583	0·04229	0·7763	0·01812
0·1274	0·1339	0·9658	0·01829
0·1034	0·1794	0·0129	0·01808
0·02703	0·02745	0·2024	0·01812
0·06443	0·06540	0·4821	0·01813

If the reaction is the decomposition of hydriodic acid and written as $2HI \rightleftharpoons H_2 + I_2$, the equilibrium constant K will be the reciprocal of the above equilibrium constant. Here, of course, the number of mols of hydrogen and iodine are equal and so the mass law equation is

$$\frac{[H_2][I_2]}{[HI]^2} = K \quad \text{or} \quad \frac{x^2}{(2a-2x)^2} = K \quad \dots \quad \dots \quad (9)\text{-XIV}$$

where $2a$ = original number of mols of hydriodic acid taken and x = the number of mols of hydrogen or iodine found at equilibrium.

(c) **Dissociation of phosphorus pentachloride**—The dissociation is represented by the equation—
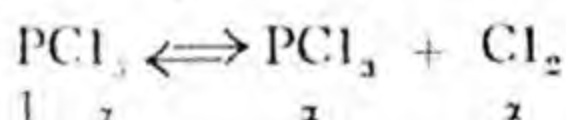
$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$1 \quad x \qquad x \qquad x$$

Let 1 mol of the pentachloride be vaporised in a total volume of V litres. It dissociates giving x mols of the trichloride and x mols of chlorine, where x is called the degree of dissociation.

The *concentrations* of PCl_5, PCl_3 and Cl_2 are $\dfrac{1-x}{V}$, $\dfrac{x}{V}$ and $\dfrac{x}{V}$

respectively. Substituting these values in the mass law equation we have

$$K_c = \frac{[PCl_3] \times [Cl_2]}{[PCl_5]} = \frac{x^2}{(1-x)V} \quad \dots \quad \dots \quad (10)\text{-XIV}$$

It is to be noted that the values of x, the degree of dissociation, depends on the total volume of the system, and consequently on the total pressure of the system. Such a system shows abnormal vapour density and x can be determined from vapour density measurements (P. 40).

The above equilibrium constant is K_c, the other equilibrium constant K_p can be calculated as follows:

Constituents	Original	At equilibrium		
	Moles	Moles	Mol fraction	Partial Pressure
PCl_5	1	$1-a$	$1-a/1+a$	$[(1-a)/(1+a)]P$
PCl_3	0	a	$a/1+a$	$[a/(1-a)]P$
Cl_2	0	a	$a/1+a$	$[a/(1-a)]P$
Total Moles at $\longrightarrow$ Equilibrium	$1+a$			

Substituting these values of partial pressures in the mass law equation, we have

$$\therefore \ K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{a^2}{1-a^2} \ P \quad \ldots \qquad \ldots \quad (11) \ XIV$$

which shows that a depends on the total pressure of the system.

Further Examples of Dissociation Equilibrium—Many other cases of gaseous dissociation equilibria have been studied and some of them involve the dissociation of one molecule into two as in the previous case, and so the same equations apply. Such cases are $NH_4Cl \rightleftharpoons NH_3 + HCl$; $COCl_2 \rightleftharpoons CO + Cl_2$; $N_2O_4 \rightleftharpoons 2NO_2$; etc.

EXAMPLE 3. *Phosphorus pentachloride is 41·7 per cent dissociated at 180°C under atmospheric pressure. Calculate the equilibrium constant using partial pressure. Also calculate the degree of dissociation at 2 atmospheres.*

The equation to be used has already been deduced [eqn. (11)]. Putting $a = ·417$ and $P = 1$, we have.

$$Kp = \frac{a^2}{1-a^2} \ P = \frac{(·417)^2}{1-(·417)^2} \times 1 = ·202.$$

When $P = 2$, a is obtained from the above eqn. by putting $Kp = ·202$ and $P = 2$, when $a = 30\%$ (probable value).

EXAMPLE 4. *Calculate the volume per cent of chlorine at equilibrium in PCl_5 under a total pressure of 1·5 atmosphere.* ($Kp = 0·202$ of the previous example).

Putting $Kp = 0·202$, and $P = 1·5$, a comes out to be 0·343. Now, according to eqn. (5)-XI, volume per cent = mol per cent = mol fraction $\times 100 = 100a/(1+a) = 25·5\%$.

Effect of Pressure on Chemical Equilibrium—In reactions having an equal number of molecules on both sides of the equation, the equilibrium is independent of the total pressure since the mass law equation contains no term involving volume or pressure. The following table compiled from Bodenstein's data for hydriodic acid formation verifies the truth of the above statement showing that the number of mols of hydriodic acid formed from one mol of hydrogen and one mol of iodine remains

approximately constant over a pressure range of half to two atmospheres.

Total Pressure :—	0·5	1·0	1·5	2 atm.
Mols HI formed :—	0·404	0·428	0·444	0·426

But, in reactions in which the number of molecules changes, in other words, where the chemical reaction is attended with a change in volume (e.g. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; $N_2 + 3H_2 \rightleftharpoons 2NH_3$, etc.) the equilibrium point shifts with a change of external pressure. Hence, the degree of dissociation of gases like phosphorus pentachloride, ammonium chloride, nitrogen tetroxide, etc., will change with external pressure at constant temperature. This is also to be expected from the law of mass action, since the equation for the equilibrium constant, K contains either a volume or a pressure term.

From a closer study of these equations, and also from experiments, it has been found that in such cases, *increase of pressure shifts the equilibrium point towards the direction in which the volume decreases, i.e., the number of mols decreases, and vice versa.* For example, pressure will favour the formation of ammonia from N_2 and H_2 since the number of mols decreases due to the reaction. The following table illustrates our point for the ammonia synthesis reaction at 500°C.

Total Pressure :	1	10	50	100	300	600 atmos.
Yield per cent ammonia :—	1	1·2	5·6	10·4	26·2	42·1

This effect of pressure on the position of equilibrium is of great importance in technical processes and will be discussed again.

Influence of Temperature on Chemical Equilibrium—The equilibrium constant, K, is a constant only at a particular temperature and usually changes its value with change of temperature. In other words, the position of equilibrium gets displaced with change of temperature. A better insight is gained by remembering that all chemical equilibria are *dynamic* in nature and are established when the forward and the backward reactions have the same speed. The effect of temperature is to change both the forward and the backward reactions but to an unequal extent with the result that the position of equilibrium gets shifted with change of temperature.

A very useful rule has been experimentally and theoretically obtained which predicts qualitatively the effect of temperature and runs thus:—*At constant pressure, the reaction which takes place with an absorption of heat is favoured by an increase of temperature, and conversely.* In other words, endothermic reactions are favoured by an increase of temperature whereas exothermic reactions have less yield at higher temperature. (For quantitative treatment *vide* end of this chapter).

The reaction, $N_2 + O_2 = 2NO - 40,140$ cals., takes place with absorption of heat and so, in the fixation of nitrogen where this

reaction is the primary one, electric are is used to obtain as high a temperature as possible. All technical processes are guided by such basic considerations and this phase of the subject will be considered again.

Since most dissociation processes are accompanied by absorption of heat, they are favoured by an increase of temperature. Thus, the colour of N_2O_4 gradually turns black with rise of temperature owing to the formaiton of NO_2 according to the eqn, $N_2O_4 = 2NO_2 - 12,260$ calories. These considerations apply only to systems in true equilibrium; the fact that ozone an endothermic compound is stabler at room temperature than say, at 300°C does not violate the above rule, since ozone at room temperature is not a system in true equilibrium.

Comparison of the effect of Temperature and Pressure—The position of equilibrium is shifted by a change of temperature or a change of pressure, but the underlying reasons are different in the two cases. In the former case, the shift is due to a change in the equilibrium constant itself, while in the latter case, the equilibrium constant is not affected, but the equilibrium point changes since the mass law equation contains volume or pressure terms.

Effect of Adding one of the Products of Reaction—Let

the reaction be $A + B \Longleftrightarrow C + D$; $\therefore K = \dfrac{[C] \times [D]}{[A] \times [B]}$. It is evident

from the form of the mass law equation that by adding a component, say, C, the numerator increases and so the denominator should increase to maintain the constant value of K, *i.e.*, the equilibrium will be displaced towards the left. We may therefore conclude that *whenever a substance participating in an equilibrium is added to the system, the equilibrium gets displaced in such a way as to tend to use up the substance added i.e.* on addition of any of the components of the left hand side of the equation, the reaction goes to the right, and *vice versa*.

It is to be noted carefully that the above rule is valid only if the volume of the system is kept constant. In case the volume is allowed to change (for example, a gaseous system at constant pressure), by introduction of one of the components the shift of equilibrium might be under some circumstances in a direction quite opposite to that required by the above rule.

Effect of Adding an Inert Gas—If a non-reacting gas is introduced into the system at constant volume (of course the pressure will change) the equilibrium constant and equilibrium point will remain unaffected because the partial pressures of the reactants and the products remain unaffected. However, if the inert gas be introduced at constant pressure (with consequent increase of volume), the equilibrium will be displaced wherever K_p is dependent on pressure, though the equilibrium constant K_p will remain unchanged because K_p is independent of change of pressure. This is a rather subtle point which could be easily brought home by a few simple calculations.

Le Chatelier's Theorem —The effect of change of pressure, temperature or of the addition of a substance as just now discussed, follows from a general rule due to Le Chatelier, which can be stated as follows: *When a system at equilibrium is subjected to a stress (such as a change of pressure, temperature or concentration), the system reacts in such a way as to tend to relieve itself of that stress.*

So, if the temperature of a system is raised by adding some heat from outside, the system will change in the direction in which it can destroy some of the heat supplied to it, and this evidently is done if a change takes place in the system which occurs with absorption of heat. So, we come to the rule that *increase of temperature favours the reaction which takes place with absorption of heat.*

If the pressure on the system is increased, the system will change in a direction in which it can release some of the additional pressure and it can do so by bringing about the reaction in the direction in which it takes place with a diminution in the number of mols, *i.e.* in the direction in which there is a decrease in volume.

If any of the components is added from outside, its concentration increases and hence, the system tends to change in such a way as to decrease the concentration of the added product. This can be done if the reaction in the other direction is favoured. So, it is seen that the theorem of Le Chatelier is in perfect accord with the observations and conclusions we have already made.

The Application of Physico-chemical Principles to Technical Reactions—From the foregoing considerations it appears that (*i*) for endothermic compounds the yield is increased by increase of temperature, (*ii*) for exothermic compounds the yield is increased by lowering of temperature, and (*iii*) in reactions entailing a contraction of volume, the yield is increased by increase of pressure.

(*a*) **Synthesis of Ammonia** —Application of these results to the synthesis of ammonia, according to the exothermic reaction—

$$N_2 + 3H_2 = 2NH_3 + 11,800 \text{ cal.}$$

would lead us to expect a greater yield at lower temperature. But in technical processes, the yield is not the only important consideration, but also the time to reach that yield. At very low temperature, though the yield may be very high the time required to reach the equilibrium would be inconveniently long. So, the reaction would be conducted at the lowest possible temperature consistent with workable reaction speed. Therefore, for every exothermic technical process there is a temperature called '**optimum temperature**' below which it is not profitable to work the process in consideration of reaction speed while above which the yield diminishes owing to a shift in equilibrium.

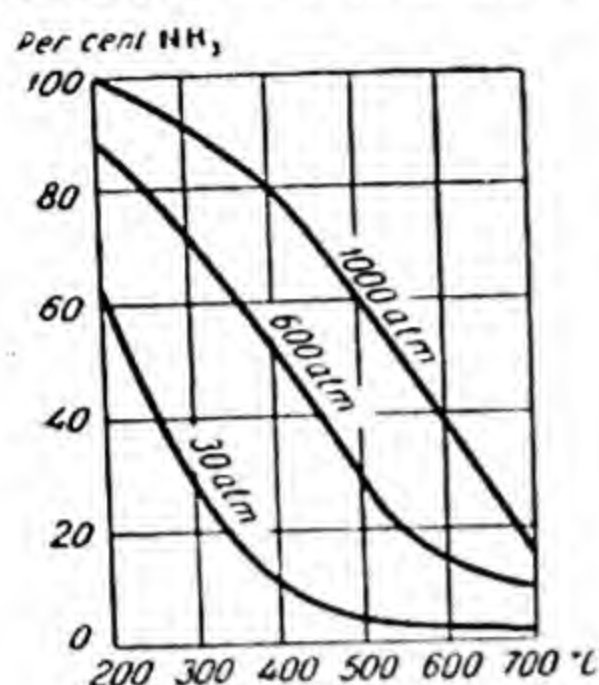Since a catalyst profoundly influences the speed of a chemical reaction but has no effect on the final position of equilibrium, a catalyst is considered more efficient, the higher the reaction speed it can produce at any given temperature. Hence, the optimum temperature would vary with the catalyst used ; for the above reaction using reduced iron and molybdenum as catalyst the optimum temperature is about 550°C.

Fig. 79.—Variation of yield of ammonia with temp. and pressure.

The reaction involves a diminution in volume and hence the yield will be higher the greater the pressure. So, the common technical process using the above reaction (*Haber's process*) uses a pressure of 200 atmospheres, though pressures up to 1000 atmospheres have sometimes been employed. The following table and the accompanying figure (Fig. 79) which gives the percentage of NH_3 formed at various temperature and pressures, illustrates the truth of the above conclusions.

Temp. °C	Pressure in atmospheres			
	10	30	50	100
350	7·73%	17·8%	25·1%	....
400	3·85	10·09	15·11	24·91%
450	2·04	5·80	9·17	16·35
500	1·2	3·48	5·58	10·40

(*b*) **Synthesis of Nitric Oxide** —The oxidation of nitrogen takes place with a large absorption of heat.

$$N_2 + O_2 = 2NO - 44,000 \text{ calories.}$$
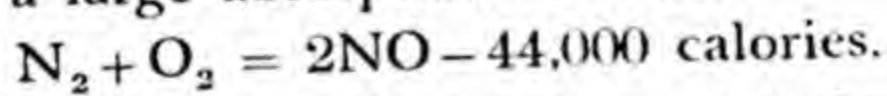
The yield, therefore, will be increased by an increase in temperature and unaffected by a change of pressure.

Not only *high temperature* but also *efficient cooling* of the products is essential. For, if the equilibrium mixture is cooled slowly, the percentage of nitric oxide will gradually decrease corresponding to lower conversion at these lower temperatures. To avoid this subsequent decomposition, the best way would be to 'chill' down the very hot gaseous products quickly to temperatures lower than 1500°C or 1000°C, where the rate of decomposition is too

Temp.	Percentage of NO
1538°C	0·07
1604°C	0·42
1760°C	0·64
2307°C	2·05
2402°C	2·23
2907°C	5·0

slow to affect the composition of the mixture. Commercial processes such as that of Birkeland and Eyde, etc. work on this principle. The adjoining table shows clearly the increasing yield with rising temperature.

(c) **Oxidation of Sulphur Dioxide**—The conversion of SO_2 to SO_3 is a strongly exothermic process.

$$2SO_2 + O_2 = 2SO_3 + 45,200 \text{ calories.}$$
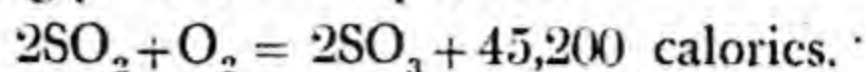
So, the yield will be greater the lower the temperature of working, and a catalyst will be considered more efficient, if it can produce suitable working speed at a lower temperature. Finely divided platinum or vanadium pentoxide has been found to be the most suitable catalyst for the process, the 'optimum' temperature being about 400°—450°C when about 99% conversion is obtained. It appears from the equation that the reaction has a possibility of higher yield at high pressure, but with the above working conditions the conversion is so complete as to leave no room for improvement of yield and hence the process is worked at ordinary pressure.

(d) **Other Technical Gas Reactions**—Similar considerations apply to all technical gas reactions, e.g. Deacon's process, oxidation of ammonia, manufacture of hydrogen, manufacture of methanol, manufacture of aviation fuel (isoctane), etc. and in all modern processes proper considerations are always given to these basic physico-chemical principles.

EXAMPLE 5. *In a mixture of N_2 and H_2 in the ratio of 1 : 3 at 30 atmos and 350°C, the percentage of ammonia under conditions of equilibrium is 17·8. Calculate the equilibrium constant of the mixture.*

Let us write the equation as $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$, and assume that the given percentage is by volume.

Since partial pressure of any component in a mixture is proportional to its percentage by volume, the partial pressure of ammonia is $0·178 \times 30$ atmos. Therefore, the partial pressure of the other two gases are $(1 - 0·178) \times 30$ atmos. But since the gases are in the ratio 1 : 3, the partial pressure of nitrogen is evidently $\frac{1}{4}(1 - 0·178) \times 30$ and that of hydrogen $\frac{3}{4}(1 - 0·178) \times 30$ atmos. Therefore, substituting these values of partial pressures into the following equation, we have,

$$\therefore K_p = \frac{P_{NH_3}}{(P_{N_2})^{\frac{1}{2}} \times (P_{H_2})^{\frac{3}{2}}} = \frac{·0178 \times 30}{(·2055)^{\frac{1}{2}} \times (·6165)^{\frac{3}{2}} \times 30^2} = 0·002697$$

EXAMPLE 6. *If a mixture of 3 mols H_2 to 1 mol N_2 react under a constant pressure of 100 atmos to form at equilibrium 0·5 mol ammonia, calculate K_p for the reaction, $3/2H_2 + \frac{1}{2}N_2 \rightleftharpoons NH_3$ at this temperature.*

Now, from the equation, 0·5 mol N_2 and 1·5 mol H_2 disappear per mol of NH_3 formed. Therefore, at equilibrium,

Mols	Mol Fraction	Partial Pressures
$N_2 : -1 - 0·25 = 0·75$	$0·75/3·5 = 0·214$	$0·214 \times 100 = 21·4$ atm
$H_2 : -3 - 0·75 = 2·25$	$2·25/3·5 = 0·644$	$0·644 \times 100 = 64·4$ atm
$NH_3 : - = 0·50$	$0·50/3·5 = 0·142$	$0·142 \times 100 = 14·2$ atm
Total Mols $= 3·50$		

$$K_p = \frac{P_{NH_3}}{(P_{H_2})^{\frac{3}{2}} \times (P_{N_2})^{\frac{1}{2}}} = \frac{14·2}{(64·4)^{\frac{3}{2}} \times (21·4)^{\frac{1}{2}}} = 0·00594$$

THERMODYNAMICS OF CHEMICAL EQUILIBRIA

Free Energy Change in a Chemical Reaction—The free energy change in a chemical reaction may be deduced in a picturesque manner due to van't Hoff with the help of his device of "equilibrium box". Take the reaction $aA + bB \rightleftharpoons cC + dD$. Let us imagine a box containing this equilibrium mixture at temperature T and fitted with four semipermeable membranes, (dotted line in the fig.) each allowing respectively only one of the four chemical species to pass through, which may be closed at will (Fig. 80). Let a mols of A and b mols of B be kept in two reservoirs, at the same temperature T, and at pressures p_A and p_B respectively. Let the partial pressures of the gases in the box be P_A, P_B, P_C and P_D. Now let us perform the following
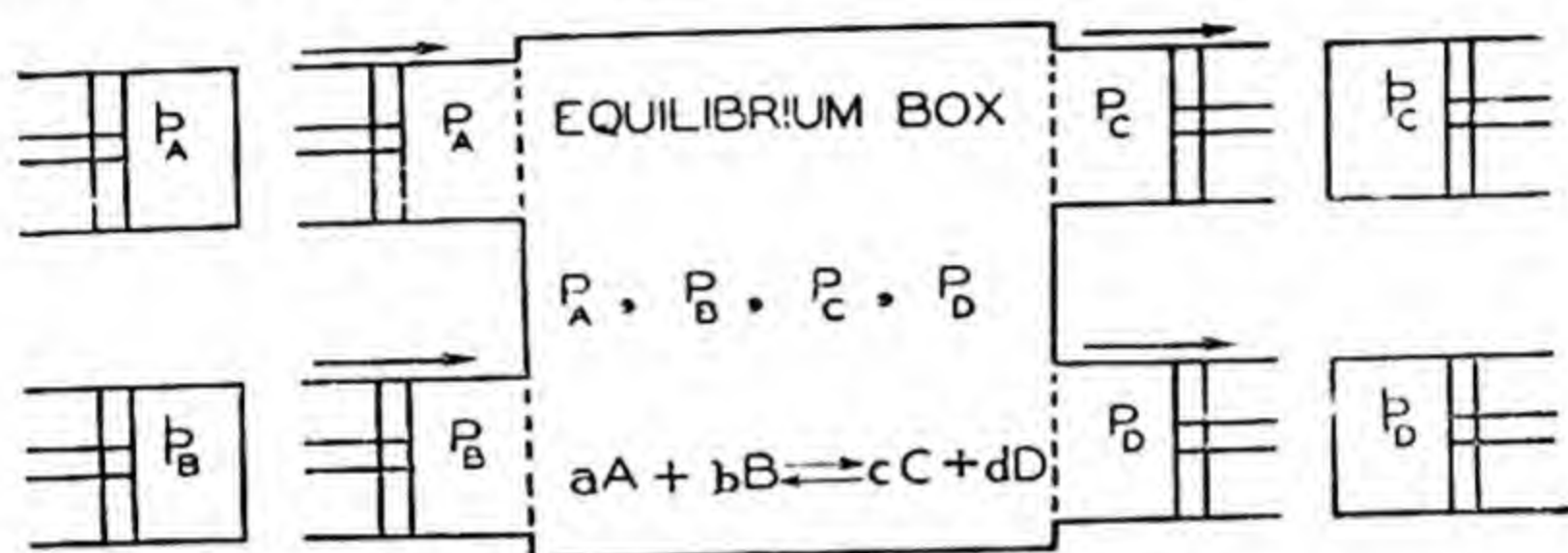
Fig. 80—Van't Hoff's Equilibrium Box.

steps. (*i*) By reversible and isothermal processes, carried out with the help of impervious pistons, the gases A and B are brought to pressures P_A and P_B respectively. The amounts of work done are $aRT \, ln \, (p_A/P_A)$ and $bRT \, ln \, (p_B/P_B)$. (*ii*) At constant pressures P_A and P_B the gases are pressed into the box through the respective semipermeable membranes. The amounts of work done are $-aRT$ and $-bRT$. (*iii*) In order that the equilibrium in the box may remain undisturbed, c and d mols of C and D, are drawn out, as they are formed, at pressures P_C and P_D. The amounts of work done are $+cRT$ and $+dRT$. (*iv*) C and D are isothermally and reversibly brought to pressures p_C and p_D, the amounts of work being $cRT \, ln \, (P_C/p_C)$ and $dRT \, ln \, (P_D/p_D)$. So, the isothermal work, w done in the conversion of a and b mols of A and B to c and d mols of C and D at temperature T is

$$w = RT ln \, \frac{P_C{}^c . P_D{}^d}{P_A{}^a . P_B{}^b} - RT ln \, \frac{p_C{}^c . p_D{}^d}{p_A{}^a . p_B{}^b} + \triangle n RT. \qquad \dots \quad (12)\text{-}XIV$$

where $\triangle n = c + d - a - b$.

∴ Net work, $w' = w - p\triangle V = w - \triangle n RT$.

Now, by definition, $-\triangle F = w'$ *i.e.* free energy change is equal to the negative of the net isothermal and reversible work done by the system (see equation 11-X). So we may write

$$-\triangle F = RT ln \ \frac{P_C{}^c . P_D{}^d}{P_A{}^a . P_B{}^b} - RT ln \ \frac{p_C{}^c . p_D{}^d}{p_A{}^a . p_B{}^b} \qquad \dots \text{(13)-XIV}$$

Now, if the initial and final partial pressures be arbitrarily fixed, say, each at unity, (*i.e.* all $p=1$ in eqn. 13) the work done and hence the decrease in free energy would be a constant for a given reaction. Calling this the standard free energy change for the reaction in question, say $-\triangle F°$, we obtain

$$\therefore \quad -\triangle F° = RT ln \left[\frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} \right] = \text{constant.}$$

$$\therefore \quad \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} = \text{a constant} = K_p \dots \qquad \dots \text{(14)-XIV}$$

So, we have thermodynamically deduced the law of mass-action. Now, combining the above equation with equation (13), we get

$$-\triangle F = RT ln K_p - RT ln \ \frac{p_C{}^c . p_D{}^d}{p_A{}^a . p_B{}^b} \qquad \dots \text{(15)-XIV}$$

This is known as **van't Hoff's reaction isotherm** and $-\triangle F$ is called the *affinity* of the reaction. Also, we have

$$\triangle F° = -RT ln K_p \qquad \dots \qquad \dots \text{(16)-XIV}$$

which gives the standard free energy change for the reaction, *i.e.*, free energy change to convert the reactants at unit pressure into the products at unit pressure. For example, $\triangle F°$ for the reaction. $H_2 + \frac{1}{2}O_2 = H_2O$ is -54.65 kcal at $25°C$ means that if a mol of hydrogen and half a mol of oxygen both at unit pressure be converted into water vapour at unit pressure at constant temperature of $25°C$, the free energy decrease or net work obtainable is 54.68 kilocalories.

Effect of Temperature on Chemical Equilibria—Differentiating equation (15)-XIV with respect to T at constant pressure and then multiplying by T we get

$$-T . \left(\frac{\partial \triangle F}{\partial T} \right)_P = RT ln K + RT^2 \left(\frac{\partial ln K_p}{\partial T} \right)_P - RT ln \frac{p_C{}^c p_D{}^d}{p_A{}^a p_B{}^b}$$

$$= -\triangle F + RT^2 \left(\frac{\partial ln K_p}{\partial T} \right)_P$$

Comparing with Gibbs-Helmholtz equation [(18)-X].

$$\triangle F - \triangle H = T . \left(\frac{\partial \triangle F}{\partial T} \right)_P , \text{ we have}$$

$$\frac{d ln K_p}{dT} = \frac{\triangle H}{RT^2} \qquad \dots \qquad \dots \text{(17)-XIV}$$

This is the desired equation in differential form, known as **van't Hoff's reaction isochore**, which correlates the temperature coefficient of equilibrium constant with the heat of reaction.

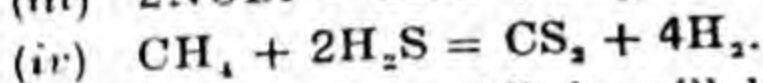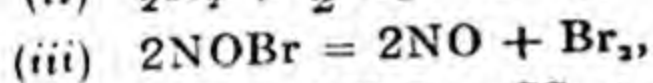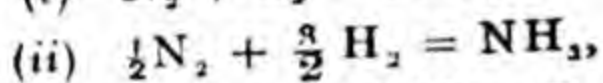Assuming $\triangle H$ to be independent of temperature we can integrate it to get the equation
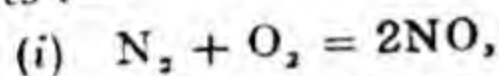
$$log \frac{K_{p_2}}{K_{p_1}} = \frac{-\triangle H}{2 \cdot 303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \ldots \quad \ldots \quad (18)\text{-XIV}$$

Hence, if we know the equilibrium constant at two temperatures, we can calculate $-\triangle H$, the heat of reaction at constant pressure. Alternatively, knowing the heat of reaction and the equilibrium constant at one temperature, we can calculate the latter at any other temperature.

Exercises

1. What are reversible and irreversible reactions? Comment on the statement, "all reactions are reversible". Can you cite any experimental proof of the dynamic nature of chemical equilibrium? How can you be sure that the given state of a system is a case of true equilibrium?

2. State the law of mass action and formulate the mass law expression for the following reactions in terms of known amounts of original reactants :—

(i) $N_2 + O_2 = 2NO$,

(ii) $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$,

(iii) $2NOBr = 2NO + Br_2$,

(iv) $CH_4 + 2H_2S = CS_2 + 4H_2$.

Discuss how these equilibria will be shifted by an increase of pressure and discuss the effect of addition of an inert gas (i) at constant vol. and (ii) at constant pressure on the yield in the above reactions.

3. Write short notes on :—(a) balanced state, (b) Le Chatelier's Principle (c) reaction isochore, (d) relation between Kp and Kc.

4. If the equilibrium constant changes ten times by a certain increase of temperature for a reaction of the type $H_2 + I_2 = 2HI$, show that for sufficiently small conversion the yield is changed $\sqrt{10}$ times under otherwise identical conditions.

5. If one mol each of acetic acid and ethyl alcohol is mixed, the reaction, $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ proceeds to 2/3 conversion. If we start with (a) 1 mol of ethyl alcohol and 2 mols of acetic acid, (b) 1 mol of acetic acid and 2 mols of ethyl alcohol and (c) 1 mol of acetic acid, 1 mol of ethyl alcohol and 1 mol of water how much ester will be present in each case at equilibrium?   [0·846 : (c) 0·542]

6. How will the above original equilibrium be affected by adding (i) 10 gms of acetic acid or (ii) 10 gms of ethyl alcohol?   [0·716, 0·729]

7. Discuss the physico-chemical principles underlying the working conditions of some important technical processes.

8. A sealed tube containing nitrogen tetroxide on gradually raising the temperature becomes almost opaque and on further raising the temperature becomes again colourless. Explain the phenomenon.

9. Iodine is partially dissociated into atoms on heating. Suppose a system containing iodine atoms and molecules (I_2) is subjected to continually increasing pressure until the new partial pressure of iodine molecules is double its original value. By what factor will the degree of dissociation and concentration of I change.   [$a_1 : a_2 = \sqrt{2} - 0.41 a_1$]

10. Explain with the help of Le Chatelier's theorem why nitrogen dioxide gas becomes lighter in colour when compressed at constant temperature.

15

11. A salt is found to dissolve in its nearly saturated solution with an increase of the total volume. Can you predict how the solubility of the salt would change if pressure is applied to the saturated solut.on.

12. Solubility of common salt increases very little with increase of temperature. What conclusions can you make concerning its heat of solution.

13. At 497°C, and under a total pressure of 261·4 mm. of mercury, N_2O_4 is 63 per cent dissociated into NO_2. What would be its degree of dissociation at the same temperature but under a pressure of 95·8 mm?
[80·4%].

14. At 250°C, and 1 atm. pressure, phosphorus pentachloride is 80 per cent dissociated. Find its dissociation constant. [80·4%].

15. When 1 gm. of PCl_5 crystals is vaporised at 182°C and 1 atmosphere, the density of the vapour referred to air is 5·08 when equilibrium is reached. Calculate a, Kc and Kp. [Given air is 14·4 times heavier than H_2.] [$a=42·5\%$; $Kc=·0059$; $Kp=·221$]

[Hint :—Determine a from $a=(D_0-D)/D$; from a, calculate Kp from $Kp=a^2P/(1-a^2)$; and Kc from the equation $Kp=KcRT$.]

16. A mixture of SO_2 and O_2 at 1 atmos in the mol ratio of 2:1 is passed through a catalyst at 1170°C at a rate sufficient for attainment of equilibrium. The exit gas, suddenly chilled and analysed, is found to contain 87% SO_3 by volume. Calculate Kp for the recation $SO_2+\frac{1}{2}O_2=SO_3$. [47·85]

17. (a) A sample of 0·127 g. iodine when heated in a quartz vessel of 225 c.c. capacity at 1000°C is found to exert a pressure of 200 m.m. Calculate the dissociation constant for the I_2 molecules and the partial pressures. [(a) 0·01954; (b) 0·201 atm.]

(b) Assuming the above value of Kp calculate the total pressure of the system if the partial pressure of atomic iodine is ·01 atm. [0·015 atm.]

18. It is found that 0·0755 gram of selenium (Se—79·2) vapour occupying a volume of 114·2 c.c. at 700°C exerts a pressure of 185 mm. The selenium is in a state of dissociation equilibrium in accordance with the reaction, $Se_6 \rightleftharpoons 3Se_2$. Calculate a, Kp and Kc.
[$a=0·597$; $Kp=0·1755$; $Kc=2·756\times10^{-3}$]

[Hint :—Calculate apparent density (D) from the eqn. $D=PM/RT$ (eqn. 4–II) and then get a form $a(n-1) = (D_0-D)/D$ where $n=3$].

19. If a is the degree of dissociation of NH_3 at a pressure P prove that $a=1/(1+1·30P/Kp)$.

20. If the difference between heat of reaction at constant volume and that at constant pressure for an endothermic reaction at 25°C is 1190 calories. what is the value of the ratio Kp/Kc? [$RT^2=(595·4)^2$]

21. Equilibrium constant (Kp) for the reaction $2H_2S=2H_2+S_2$ is ·0118 at 1065°C and heat of dissociation is −42400 calories. Find the equilibrium constant at 1132°C. [0·0251]

22. Equilibrium constants (Kp) for the reaction $\frac{3}{2}H_2+\frac{1}{2}N_2=NH_3$ are ·0266 and ·0129 at 350°C and 400°C respectively. Calculate the heat of formation of gaseous ammonia. [12,140]

23. Twenty grams of hydriodic acid are heated to 327°C in a bulb of 1 litre capacity. Calculate the volume percentages of H_2, I_2 and HI at equilibrium given that the mass law constant for the squation $2HI=H_2+I_2$ is 0·0559 at 327°C, when the concentrations are expressed in moles per litre. [HI=67·9 per cent; $H_2=I_2=16·05$ per cent.]

(Hint :—Calculate x from the eqn. $x^2/4 (a-x)^2=K$ deduced on P 217. For a gas mixture, percentage by volume is equal to mol. per cent i.e. mol-fraction $\times100$ i.e. in this case, $x/2a$ for H_2 and I_2.]

CHAPTER XV

HETEROGENEOUS EQUILIBRIUM

General—Any portion of the physical world under consideration limited by real or imaginary boundary is called a system. In any system, each *physically distinct and mechanically separable* portion of matter which is itself *homogeneous* and uniform in composition is called a *'phase'*—a term, which we have often used in the previous chapters. ⟨Any system consisting of more than one phase is called a heterogeneous system.⟩ Thus, if we have some water and water-vapour in a vessel, it is a heterogeneous system consisting of two phases, a liquid phase (water) and a gaseous phase (water-vapour.) The system obtained by heating calcium carbonate is a heterogeneous one consisting of three phases, two solid phases ($CaCO_3$ and CaO) and one gaseous phase (CO_2).

Law of Mass Action and Heterogeneous System—In applying the law of mass-action to cases of heterogeneous equilibrium, especially to systems which consist of solid phases, one is confronted with the difficulty of what meaning is to be attached to the active mass of a solid. The difficulty can however be surmounted by supposing that *the active mass of a solid is constant at a definite temperature independent of the amount of solid present.*

We may regard the matter from a different view-point. It is a well-known fact that at constant temperature, a liquid has got a definite vapour-pressure independent of its mass. Similarly, we may regard that all solids have a definite vapour-pressure of its own independent of its amount and so, the gaseous phase contains the solid in the vapour state with a negligibly small but *constant* partial pressure. In fact, most solids at high temperature and some solids *e.g.*, metallic cadmium, bismuth, etc. even at ordinary temperature have sufficient vapour pressure to be experimentally demonstrated. We may, therefore, regard it as a homogeneous equilibrium in the gas phase, in which the *solids are present with a constant partial pressure or active mass.* With this 'proviso' the law of mass action can be applied to heterogeneous systems, and some very interesting results can be deduced.

Dissociation of Calcium Carbonate—If calcium carbonate is heated in a closed space a portion of it usually decomposes forming calcium oxide (solid) and carbon dioxide (gas) and ultimately an equilibrium is set up according to the equation,

$$CaCO_3 \rightleftharpoons CaO + CO_2$$
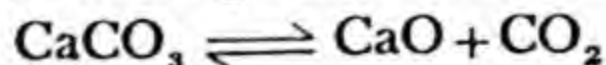
The system consists of *three phases*, two solids and one gas and we may regard, as just now discussed, that the active masses

or partial pressures of the solids are constant. Therefore applying the law of mass action, we have

$$K = \frac{P_{CaO} \times P_{CO_2}}{P_{CaCO_3}} \text{ or } P_{CO_2} = K \frac{P_{CaCO_3(s)}}{P_{CaO(s)}} = \text{constant.} \quad \ldots (1)\text{-XV}$$

The very interesting and unexpected result comes out that *the pressure of carbon dioxide is constant at constant temperature.* This equilibrium pressure of carbon dioxide, which is constant at constant temperature, is called, on account of its similarity with the vapour pressure of liquids, *dissociation pressure* of calcium carbonate. At every temperature, the system will attain its corresponding dissociation pressure and then it is impossible by any means, even by adding to the system, lime, $CaCO_3$ or CO_2 from outside to change the dissociation pressure. Any added lime or $CaCO_3$ will remain unchanged, and CO_2, if added will combine with free lime until the pressure falls down to the dissociation pressure. This is the reason why in lime-kilns, the evolved gas is continuously removed, so that the pressure of carbon dioxide falls below the dissociation pressure. The system was first investigated by Debray (1867) and all the above deductions were verified. Some recent data for the dissociation pressures of calcium carbonate at different temperatures are given in the accompanying table.

Temperature °C	Dissociation Pressure, mm.	Temperature °C	Dissociation Pressure, mm.
500	0·073	850	372
600	1·84	900	793
700	22·2	950	1577
750	63·2	1000	2942
800	167·0	1200	21797

This type of results is valid for any solid substance, which reversibly decomposes to a number of products, only one of which is gaseous. Some illustrative examples of such reactions are—

    (a) $BaO_2 \rightleftharpoons BaO + \frac{1}{2}O_2$ (Brinn's Process)

    (b) $2\ CuO \rightleftharpoons 2Cu + O_2$

    (c) $HgO \rightleftharpoons Hg + \frac{1}{2}O_2$

    (d) CaC_2O_4 (Ca-Oxalate) $\rightleftharpoons CaCO_3 + CO$

    (e) KH (Pot. Hydride) $\rightleftharpoons K + \frac{1}{2}H_2$

    (f) $2NaH_2PO_4 \rightleftharpoons Na_2H_2P_2O_7 + H_2O$

    (g) $NiBr_2.2NH_3 \rightleftharpoons NiBr_2.NH_3 + NH_3$.

Variation of Dissociation pressure with Temperature— Since the dissociation pressure, P is equal to the equilibrium constant K_p, and since the variation of K_p with temperature is given by equation (18)-XIV, we can substitute P for K_p, when we obtain

$$\log P = \frac{-\triangle H}{2 \cdot 303 R} \frac{1}{T} + \text{Const.} \quad \ldots \qquad \ldots \quad \text{(2)-XV}$$

i.e. logarithm of the dissociation pressure when plotted against $1/T$ gives a straight line and the slope is equal to $- \triangle H / 2 \cdot 303 R$ where $- \triangle H$ is the heat of dissociation. So, from the above data we can calculate the heat of dissociation of calcium carbonate.

EXAMPLE 1.—*Using the above data for 500° and 600°C, calculate the heat of dissociation of calcium carbonate in this range.*

From equation (2), we have

$$\log (P_1 / P_2) = \frac{\triangle H}{2 \cdot 303 R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad \ldots \qquad \ldots \quad (2a)\text{-XV}$$

Substituting values, we get

$$\log (1 \cdot 84 / 0 \cdot 073) = [\triangle H / (2 \cdot 303 \times 2)] \times [(600 - 500) / 773 \times 873)]$$

or $\triangle H = + 44,100$ calories. $\therefore$ Heat of dissociation is $-44,100$ calories.

Dissociation of Ammonium Hydrosulphide

—If solid ammonium hydrosulphide is heated, it dissociates forming two gaseous products, ammonia and hydrogen sulphide according to the equation:—$(NH_4)HS \rightleftharpoons NH_3 + H_2S$. Applying the law of mass action,

$$\frac{P_{NH_3} \times P_{H_2S}}{P_{(NH_4 HS)}} = K \; ; \text{ but, } P_{(NH_4)HS} \; (solid) = \text{Constant.} \qquad \ldots \quad (3)\text{-XV}$$

$$\therefore \quad P_{NH_3} \times P_{H_2S} = K.$$

So, we arrive at the result that in the gaseous mixture *the product of the partial pressures of ammonia and sulphuretted hydrogen is constant at constant temperature*—a relation which has been experimentally verified.

Dissociation of Salt Hydrates

—If a quantity of $CuSO_4, 5H_2O$ (*blue vitriol*) is kept in a desiccator connected to a manometer, it would be seen that the manometer indicates a constant pressure, as long as the temperature is constant. The reason for this is that $CuSO_4, 5H_2O$ dissociates giving water vapour and a solid lower hydrate $CuSO_4, 3H_2O$ according to the equation—

$$CuSO_4, 5H_2O \rightleftharpoons CuSO_4, 3H_2O + 2H_2O$$
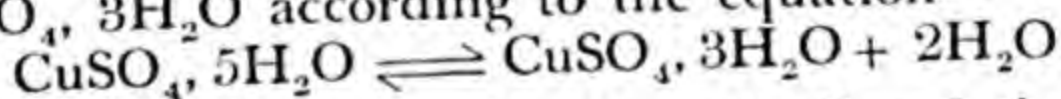
The case is similar to the thermal dissociation of calcium carbonate to form one solid (CaO) and one gas (CO_2) where it has been shown that the pressure of carbon dioxide remains constant. So, here also the pressure of water vapour in the system would be constant; the mass law equation for the system is

$$\frac{P^2_{H_2O} \times P_{CuSO_4, 3H_2O}}{P_{CuSO_4, 5H_2O}} = K$$

or, $P_{H_2O} = $ constant. $\ldots$ (4)–XV

N.B. It should be pointed out that this constant pressure of water vapour is not due to either the pentahydrate or the trihydrate, but is a property of the system as a whole consisting of the three phases, the pentahydrate, the trihydrate and the water vapour.

At 50°C, the vapour pressure of the pentahydrate—trihydrate system is 47 mm. As more and more water leaves the system,

the pressure nevertheless remains constant at 47 mm until the whole of the salt is converted into trihydrate when the pressure suddenly falls to 30 mm. The reason for this is that as soon as the whole of copper sulphate is converted into the trihydrate the above equilibrium loses its significance and now a new equilibrium is established due to the dehydration of the trihydrate to monohydrate according to the equation—
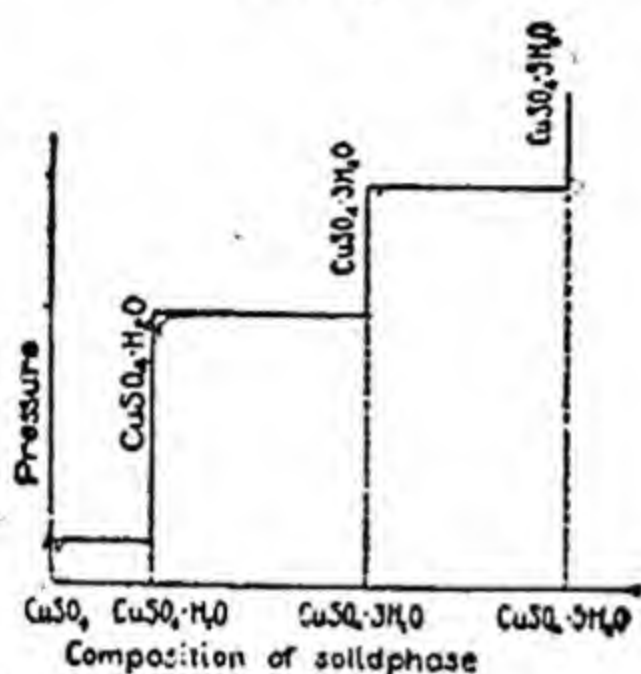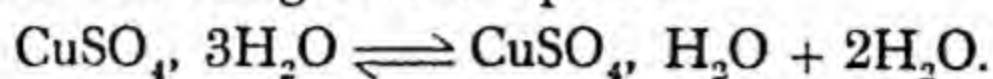
$$CuSO_4, 3H_2O \rightleftharpoons CuSO_4, H_2O + 2H_2O.$$

CuSO₄ CuSO₄·H₂O CuSO₄·3H₂O CuSO₄·5H₂O
Composition of solidphase

Fig.81—Dehydration Curve
for Blue Vitriol

Here again the vapour pressure of water vapour remains constant at 30 mm until the whole is converted into the monohydrate, when the pressure falls to 4·5 mm due to a new equilibrium, $CuSO_4, H_2O \rightleftharpoons CuSO_4 + H_2O$ and remains at this value as long as there is water vapour in the system. The above results are graphically represented in the accompanying figure where the pressure is plotted as ordinate and the composition of the solid phase as abscissa. It will be observed that the pressure suddenly drops whenever the composition of the solid phase is just the same as one of the participants in the equilibrium but otherwise remains constant parallel to the composition axis.

Efflorescence and Deliquescence—An insight into the phenomenon of efflorescence or deliquescence can be obtained in the light of the above knowledge. It has been found that there is a definite vapour pressure corresponding to a mixture of two hydrates. So, if the vapour pressure of the water vapour in the atmosphere exceeds this value, the lower hydrate is completely converted into the higher hydrate and the salt is a stable one. But, if the tension of aqueous vapour present in the atmosphere is less than this value, the salt gradually loses water and gets converted into the lower hydrate. This is the phenomenon of efflorescence or losing of water by a crystallised salt.

Deliquescence is the name given to the phenomenon of absorption of water by a salt and the solution of the salt in the water absorbed. A solid will deliquesce in moist air if the pressure of the water vapour present in the atmosphere is greater than the vapour pressure of the saturated solution of the solid. The average pressure of water vapour present in the atmosphere is less than 15 mm, while the vapour pressure of a saturated solution of CaCl₂ is only 7·5 mm. and so, the salt is deliquescent. It is thus quite possible that a salt which is ordinarily stable may become temporarily deliquescent during the rainy season when the air becomes too moist.

Action of Steam on Heated Iron—When steam is passed over red hot iron hydrogen is obtained; but the reaction is never complete, since some steam is always obtained along with the hydrogen gas. The true explanation is that the reaction is a case of *heterogeneous reversible* reaction represented by

$$4H_2O + 3Fe \rightleftharpoons Fe_3O_4 + 4H_2; \text{ or } \frac{P_{H_2}}{P_{H_2O}} = \text{constant} \qquad (5)\text{-XV}$$
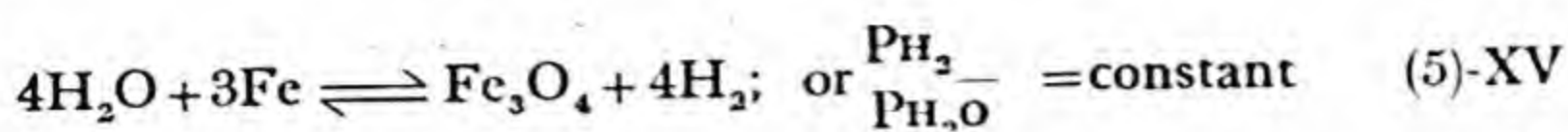
By applying the law of mass action and regarding the active mass of solids to be constant, we at once come to the conclusion that *the ratio of the pressure of hydrogen to the pressure of steam is a constant* at any given temperature. Hence, the conversion of steam to hydrogen by the above reaction can never be complete and the same final state will be reached whether we start with iron and steam or with Fe_3O_4 and hydrogen or with any other mixture of the above components.

PHASE RULE & PHASE EQUILIBRIA

Introduction—The equilibrium in a system consisting of a number of phases is however very conveniently studied with the help of the phase rule, which was thermodynamically deduced by Willard Gibbs in 1876. Before the rule can be stated formally the terms phases, components and degrees of freedom need be explained.

Phases—We have already defined the term phase as *each physically distinct portion of matter which is itself homogeneous and uniform in composition and is separable from other parts by distinct boundary surfaces.* Gases being mutually miscible in all proportions, there can be only one gaseous phase in any system. Liquid phases are as many as there are separate liquid layers. Except solid solutions all different kinds of solids form different phases. Thus, at the triple point of the water system, there are three phases, ice, liquid water and vapour. The system, $CaCO_3$ (s) $\rightleftharpoons$ CaO(s) + CO_2, consists of three phases—two solid phases and one gaseous phase.

Components—*The number of components is defined as the smallest number of independently variable constituents starting from which the composition of each phase can be expressed directly or in the form of a chemical equation.*

The water system, for example, is a one-component one, since each phase ice, liquid water or vapour is essentially water in composition. The case is the same with the sulphur system. But consider the case of dissociation of calcium carbonate according to the equation, $CaCO_3 \rightleftharpoons CaO + CO_2$. The system has got two components because two of the molecular species involved in the equilibrium in arbitrarily taken proportions can represent the composition of each of the three phases. For example, taking CaO and CO_2 as the components,—of the three phases, the composition of the $CaCO_3$ phase is simply an equimolecular mixture—*e.g.* $xCaO + xCO_2$; the composition of each of the other phases is that of only one of the components *i.e.* either CaO or CO_2 as the case may be. Exactly similar is the case of any solid which reversibly dissociates into another solid and a gas, for example,

$$CuSO_4 . 5H_2O(s) \rightleftharpoons CuSO_4 . 3H_2O (s) + 2H_2O (g)$$
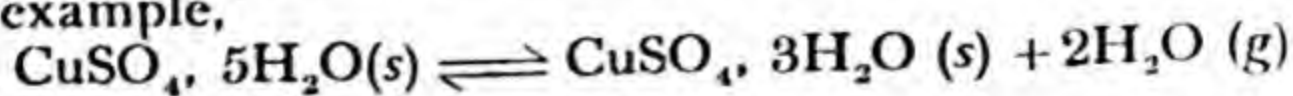
If however a solid dissociates into a number of gaseous substances e.g. $NH_4Cl \rightleftharpoons NH_3 + HCl$, the number of components is only one, because the composition of the dissociated vapour is in essense the same as that of the undissociated substance, so long the gaseous products of dissociation are present in stoichiometric proportion. In case however, NH_3 or HCl is introduced from without, the above argument does not apply and the system becomes a two-component one.

It should be pointed out in this connection that as far as phase rule is concerned, the relevant quantity is the *number* of components and not the components. The former is a unique property of the system and not the latter. For example, in the calcium carbonate system the number of components is two, but we may with equal justification call any two of CaO, CO_2 and $CaCO_3$ as components. So, the question, "which are the components in a given system?" has no unique answer and so cannot be unambiguously met. Taking the extreme view we may with perfect justice call even say, calcium and oxygen as the two components of the calcium carbonate system because if we fix the percentage of these two elements in any phase the percentage of all other elements in the same phase becomes fixed.

Degrees of Freedom—*The number of degrees of freedom of a system is the minimum number of variable factors such as temperature, pressure and concentration, which can completely define the equilibrium of a system.*

For example, consider the system, water—water vapour. So long the temperature is constant, the pressure cannot be changed without vitally disturbing the equilibrium of the system. If an attempt is made to increase the pressure of the system by increasing the external pressure, the vapour phase disappears completely producing an altogether new system. So, the system, water—water vapour is said to have one degree of freedom, or more commonly, to be univariant. Consider the triple point ice-water-vapour: this is zero-variant since neither temperature nor pressure can be changed without causing one of the phases to disappear. An ordinary gas is a bivariant system, since its temperature as well as pressure can be fixed at any arbitrary value (within limits, of course).

The Phase Rule—The rule can be stated as follows: *The sum of the number of phases and the degrees of freedom of any system exceeds the number of components by two, provided no surface effect, gravitational effect, etc. are present,* or stated in symbols,

$P + F = C + 2$, or, the more usual form, $C - P + 2 = F$ ... (6)-XV

where C is the number of components, P the number of phases and F the degrees of freedom.

Applications of Phase Rule—Applying the equation to any one-component system, say, water we find that when there are

two phases present (*i.e.* C=1 & P=2), the system is monovariant (F=1). At the triple point when the number of phases are three (*i.e.* C=1, P=3), the degree of freedom is nil (F=0). In other words, for systems, viz., ice-vapour, water-vapour or ice-water, every temperature has got a definite vapour pressure ; the non-variant system, ice-water-vapour however, can exist at only one fixed temperature. All these deductions agree with our experience with this system, and will be discussed with reference to its phase diagram as also that of sulphur in detail.

On application to the two-component system, $CaCO_3 \rightleftharpoons CaO$ $+ CO_2$, we find that so long there are three phases (*i.e.* C=2, P=3, the degree of freedom is unity. In other words, if one of the variables, say, temperature is kept constant all other factors such as pressure, concentration, etc. have to adjust themselves to constant values. This is in harmony with our experience and with the deduction of the law of mass action. The same arguments and results are valid *in toto* for the dehydration of salt hydrates.

Phase Diagram of Water—For simple systems the phase equilibrium is easily studied with the help of the vapour pressure—temperature diagrams. The diagram for water is shown schematically in Fig. 82. The curve AO (full line) is the vapour pressure curve of ice. At even very low temperatures ice has a definite vapour pressure which increases along the curve AO with rise of temperature. At 0°C, or more accurately at 0·0075°C (point D) ice begins to melt and so long ice and water are co-existing the temperature remains constant at 0·0075°C. This point O is called a triple point, since three phases. ice, water and vapour are simultaneously in equilibrium. When all the ice is melted, on further rise in temperature the vapour pressure increases along the curve, OB, the vapour pressure curve of liquid water. The graph OB terminates at the point B, the critical temperature (374°C) (critical pressure is 218 atm. and critical density is 4·4 gm/cc), above which temperature the distinction between the liquid and vapour vanishes.

The dotted portion OA, which is the continuation of the curve BO below 0°C, is the vapour pressure curve of water when supercooled below 0°C. This curve runs above the vapour pressure curve for ice in harmony with the fact that ice is stabler than water below 0°C. The curve OC represents the change of melting point of ice with pressure.

Fig. 82—Phase diagram of water (*not to scale*)

It is inclined towards the pressure axis in conformity with the well-known fact that the melting point of ice is lowered by an increase of pressure.
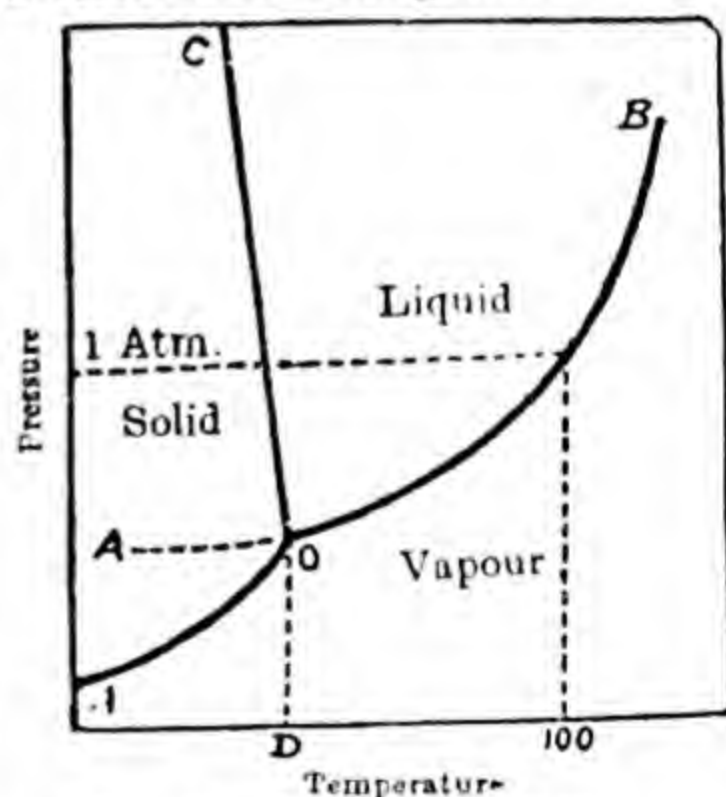
The curves divide the whole region into three portions in each of which, as indicated in the figure, only one phase is present. These vapour pressure curves are the common lines of intersection of these regions and hence along them two phases are in equilibrium. At the triple point O, three phases co-exist in equilibrium.

The phase diagram clearly indicates the conditions under which a phase is stable or not. For example, we can immediately conclude that at any definite temperature the vapour pressure of water (or ice) is fixed since any ordinate cuts the curves at one point only. The curves also clearly show that for the ice—vapour or the water—vapour system by raising or lowering the temperature at constant pressure, or by changing the pressure at constant temperature one of the phases disappears, since, by such movement on the graph we pass on to the uniphasic regions; also, since the two curves, AO and CO intersect at one point, there is only one triple point for the system.

Principle of Sublimation—From the above diagram it is clear that if a vapour below its triple point pressure (OD) is cooled it will be directly converted to the solid state. For water, the triple point pressure is 4·6 mm.; hence, if the partial pressure of water-vapour in the atmosphere falls below this value, the water-vapour will be condensed directly into the solid state (*hoar-frost*) when the atmosphere gets sufficiently cooled. The reverse is also equally true. If a solid is heated and the vapour pressure above it is not allowed to exceed the triple point pressure, the solid will be directly converted to the vaporous state. The above is the principle of sublimation. The triple point of iodine is at 90 mm pressure and 114°C. So, if iodine is slowly heated below 114°C, the solid vaporises and the vapour if cooled recondenses to the solid state. If however, the heating is done rapidly, particularly in an almost closed space, such that the vapour can neither pass out quickly nor get diluted with air, the vapour pressure eventually exceeds 90 mm and the iodine is found to melt to a mobile liquid.

For most substances the triple point pressure is far less than the atmospheric pressure and this explains the relative rarity of substances sublimable at ordinary pressure. For those substances, however whose triple point pressures exceed one atmosphere, the condition for sublimation is automatically maintained and hence they pass directly into the vapour state on heating. This is the case with *solid carbon dioxide*,—commercially known as '*dry ice*' and extensively used for refrigeration by ice-cream vendors,—whose triple point pressure is at over 5 atmospheres. Hence, the '*dry ice*' passes directly into the vaporous state and thus is free from the messiness due to liquid formation associated with ordinary refrigerants like ice.

The Sulphur System—Another one-component system which

is slightly more complex than the previous one is the sulphur system, the phase d.a-gram of which is shown in Fig. 83. AB is the vapour pressure curve of rhombic sulphur and BD that of monoclinic sulphur, the point B (95·51°) being the transition point between the two allotropic forms. At B both rhombic and monoclinic sulphur have the same vapour pressure and so, can co-exist along with their vapour. Hence, the point B is a triple point. D (119·28°) is the melting point of monoclinic sulphur and DE is the vapour pressure curve

Fig. 83—Phase diagram of Sulphur

of liquid sulphur. The lines BF and DF represent the change in transition temperature and melting point respectively with pressure and these two lines meet at F (151°C, 1290 atm.). So, F is again a triple point where rhombic, monoclinic and liquid sulphur are co-existent in stable equilibrium.
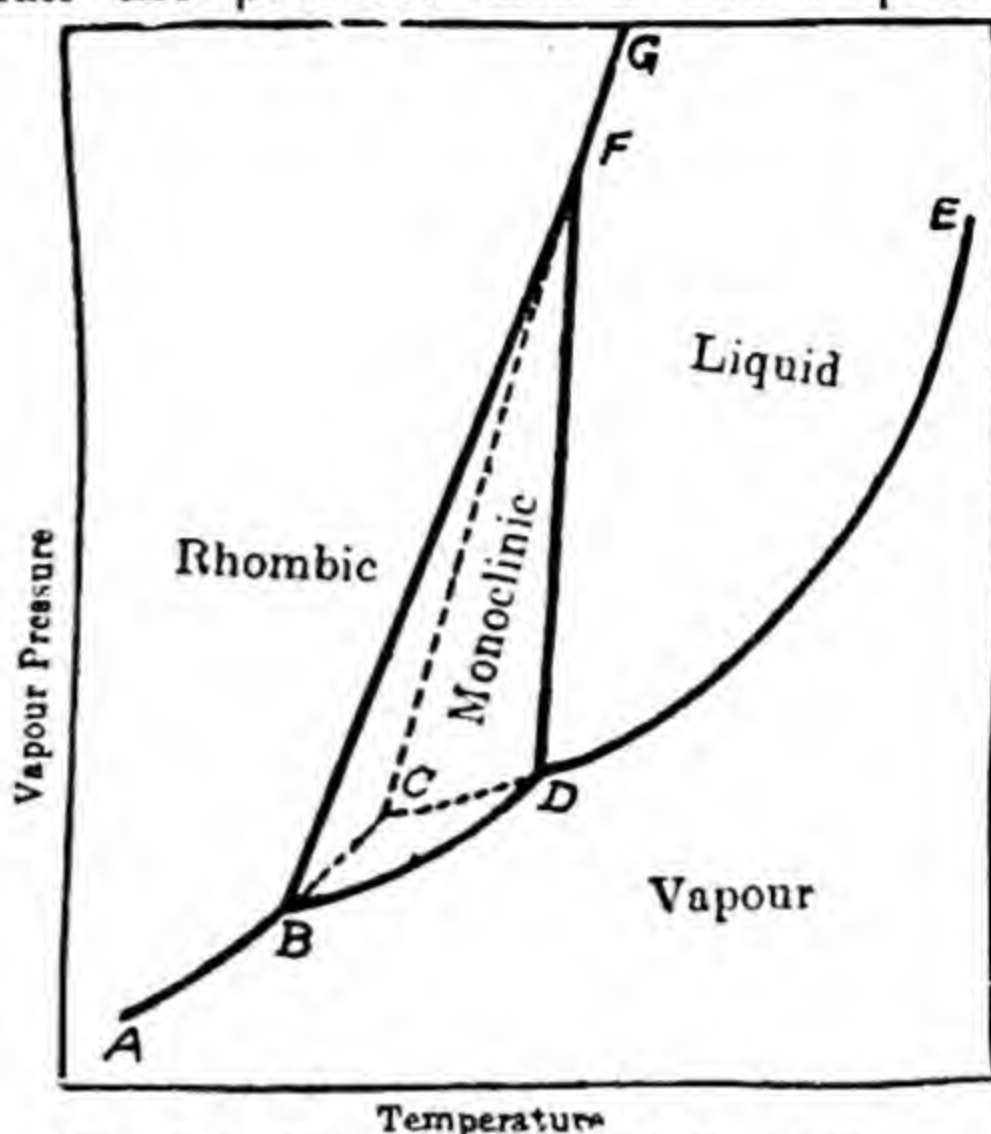
The transformation rhombic→monoclinic is rather slow and so if rhombic sulphur is quickly heated it follows the curve BC and melts at C (112·8°), the point of intersection of the vapour pressure curves of rhombic sulphur and liquid sulphur both being extended in the unstable region. However, these are essentially unstable systems tending to revert to the stable forms, and hence they are represented by dotted curves. There are in all three stable and one unstable triple points and nowhere there are four phases co-existing in equilibrium.

The above behaviour of sulphur is in perfect accord with the phase rule according to which the triple points should be zero-variant (F = C − P + 2 = 1 − 3 + 2 = 0) and the biphasic systems will be univariant (F = C − P + 2 = 1 − 2 + 2 = 1). We have already seen that in this system (as also in the previous one-component system, e.g. water) the triple points are mere points i.e. non-variant, and whenever two phases exist in equilibrium, either temperature or specific volume completely and uniquely determines the system i.e. the system is monovariant in perfect accord with phase rule.

The diagram also shows that under ordinary pressures the solid which separates on cooling liquid sulphur is the monoclinic variety as indicated by the line FD, but at pressures higher than that indicated by F, the rhombic variety is the one to separate along FG. This explains the extensive occurrence of rhombic

variety in nature and suggests that they were formed by crystallisation from molten sulphur under pressure.

Phase Equilibrium of Salt Solutions—*Phase Rule Considerations*:—We now come to the considerations of a two-component system formed by dissolving a salt in water. According to the phase rule, so long there are only two phases, the solution and the vapour, the degrees of freedom are 2, *i.e.* we can arbitrarily change any two of the variables, say, temperature and concentration. But as soon as there is another phase, say a solid phase, the system becomes univariant *i.e.* if the temperature is fixed, all other factors *viz.*, concentration and pressure admit of no variation. In other words, for each concentration of the solution there is a definite temperature at which a solid separates out of the system. And it does not matter which of the components (the salt, or ice, or any of their solid solutions or hydrates) separates as the solid phase. When the solid solvent separates, the solution is said to freeze while if the salt separates out, the solution is called a saturated one. We now proceed to discuss a typical system.

Freezing of Salt Solutions. General Description—If a dilute solution of a salt, say, potassium iodide is cooled, the solution begins to freeze at a temperature slightly lower than 0°C with separation of pure ice since the F. P. of a solution is lower than that of the pure solvent. As more and more ice separates, the solution becomes gradually richer in the salt and the freezing point goes on continually decreasing, since the freezing point of a concentrated solution is lower than that of a dilute solution. Thus, there is a *progressive lowering of freezing point* along the curve AC (Fig. 84) and on cooling ice goes on separating until the composition, C is 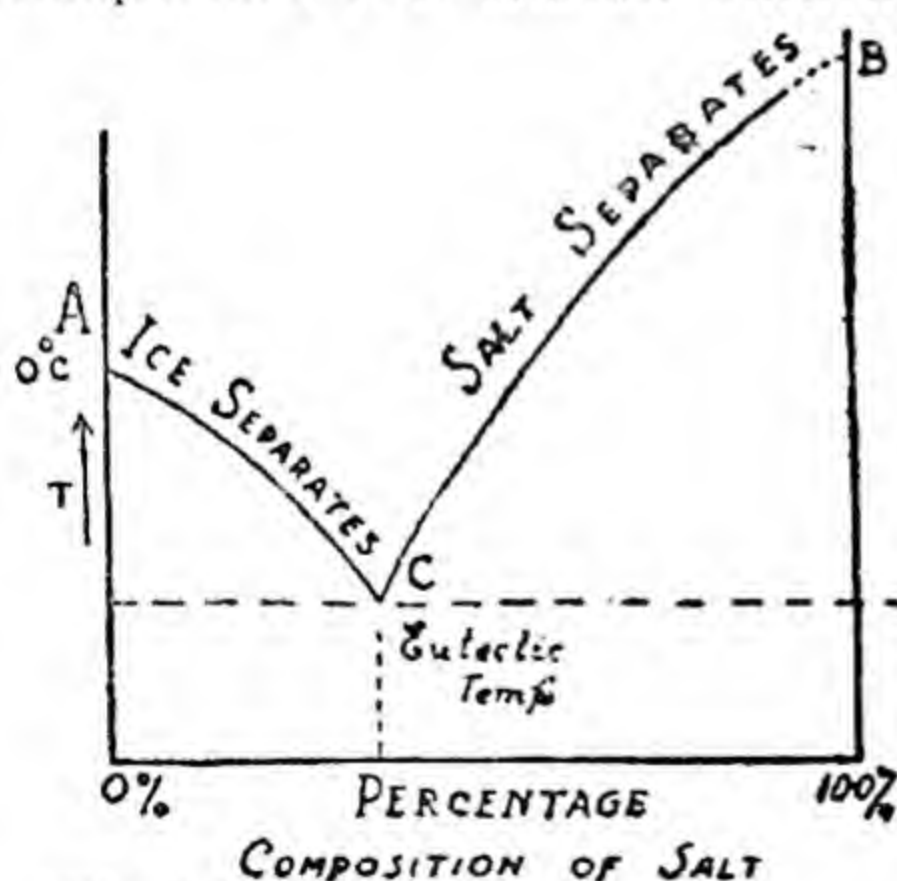reached when the solution becomes saturated with respect to the solid salt. On abstracting more heat, *the solution, C freezes as a whole at constant temperature unchanged in composition.* This lowest possible freezing point of a solution at which the solution freezes 'en masse' is called the eutectic temperature and the solid phase which separates during freezing at the eutectic point is hence, called an 'eutectic mixture'; and in this particular case of salt and water is called a 'cryohydrate.' It was formerly believed that *cryohydrates or eutectic mixtures* were definite chemical compounds but this idea is ruled

Fig. 84—Freezing Curve of Salt Solutions

out on the grounds that (*i*) the salt and water are seldom present in a molecular ratio, (*ii*) the composition of the cryohydrate is changeable with external pressure and (*iii*) the cryohydrates appear heterogeneous under the microscope.

The eutectic point is an invariant point, similar to the triple point in one-component systems ; this follows from phase rule because here the $C = 2$, $P = 4$ and therefore, $F = 2 - 4 + 2 = 0$.

For KI solution, the eutectic point, C corresponds to 52%KI. If a solution stronger than 52% is cooled, it will freeze along the curve BC, but during the freezing the solid which separates is not pure ice but is pure potassium iodide. Since the solid salt is in equilibrium with the solution along BC, BC is evidently the solubility curve of the salt. The solution, therefore, gets continually poor in KI until it reaches the temperature and composition corresponding to the point C along the curve BC. When the point C is once reached the solution freezes as a whole to form the *cryohydrate*. We may summarise the results as follows : —

If a *dilute* salt solution is cooled *ice separation* with progressive lowering of F.P. occurs until the eutectic point is reached, when it freezes as a whole.

If a solution *stronger* than the eutectic composition is cooled, the *salt separates* out during cooling until the eutectic composition is reached when it freezes as a whole.

If a solution of *eutectic composition* is cooled, the solution freezes *unchanged in composition* at the eutectic temperature.

The above is the simplest type of curve obtained for many salt solutions *e.g.* KCl-water, NaCl-water, etc. where no hydrate separates as a distinct phase as well as for many pairs of molten metals *e.g.* lead-silver, zinc-cadmium, etc. Many alloys are in fact, eutectic mixtures mixed with more or less quantities of one of the pure metals.

Simple Fusibility Diagrams of Alloys—As mentioned in the previous section some alloys show the above type of simple freezing point diagram called fusibility diagrams for alloys. Fig. 85 shows such a diagram for the system bismuth-lead.

The eutectic point in this system is 140°C and occurs at a composition of 40 per cent cadmium. So if a liquid alloy containing less than 40 per cent cadmium is cooled, pure bismuth would separate along the line AC until the eutectic composition and temperature, *i.e.* the point C is reached. If a richer alloy is cooled, pure cadmium would separate along BC until the point C is again reached when it will congeal as a whole. If an alloy of eutectic composition be cooled, it would freeze as a whole at 140°C. The solid alloy if polished, etched and examined under the microscope, would appear as a conglomerate of tiny crystals of bismuth and cadmium closely intergrown into one another.

Magnesium —Lead system gives a slightly more complex fusibility diagram, (Fig. 86) which has a maximum at the point C.

Such maximum can be interpretated by the phase rule as corresponding to a definite chemical compound, in this case Mg_2Pb, and the fusibility diagram is merely two simple fusibility diagrams combined into one, viz. that of Mg and Mg_2Pb and of Mg_2Pb
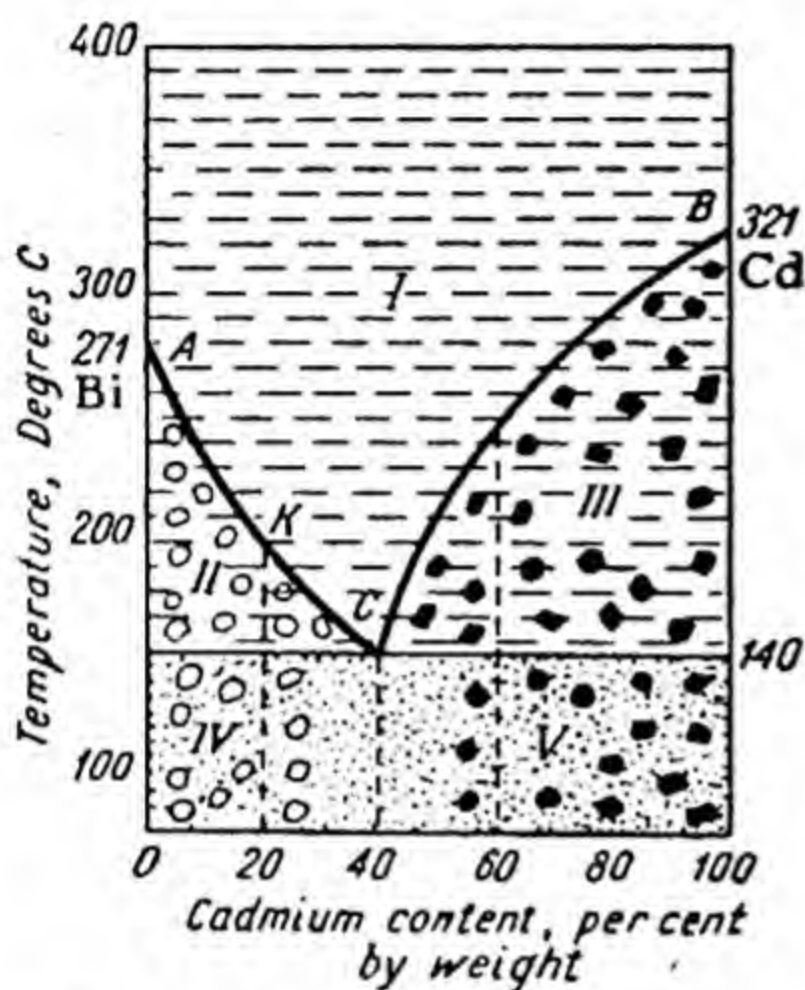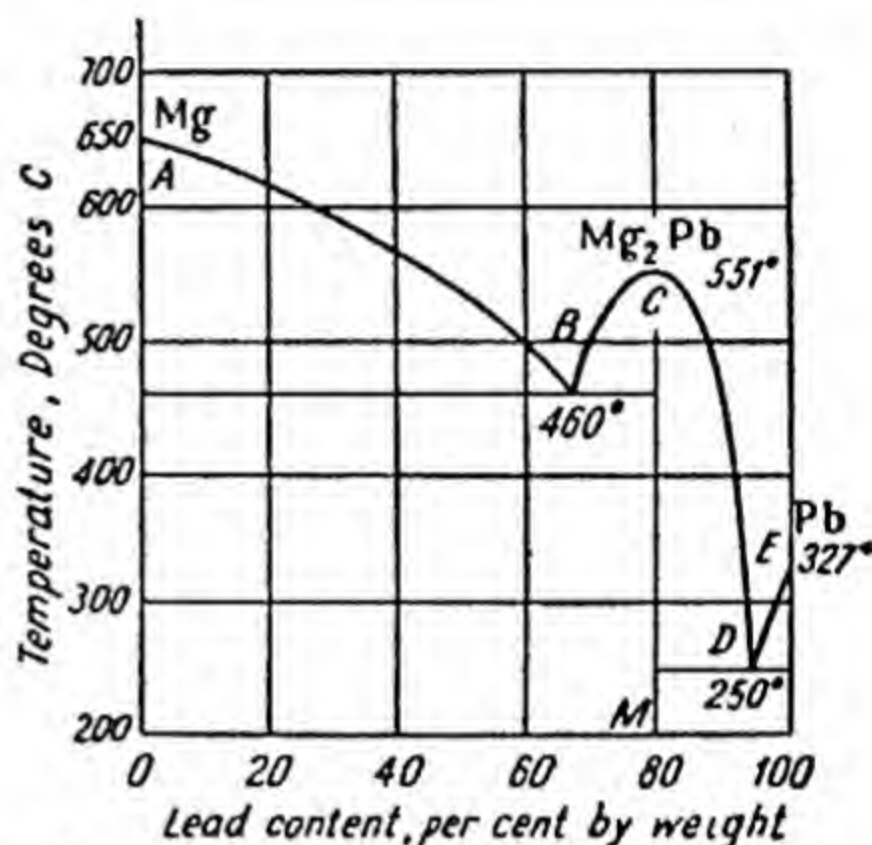

Fig. 85—Fusibility diagram of
Bismuth-Lead

Fig. 86—Compound Formation
in Mg—Pb system

and Pb. The interpretation of each of these portions is similar to the previous diagram and introduces nothing new in principle and application except that one of the constituents is not a pure metal but is an intermetallic compound.

Exercises

1. State fully the action of heat on calcium carbonate.

2. Describe the phenomena that you will observe when the following substances are progressively cooled :—(a) a dilute solution of sodium chloride and (b) a concentrated solution of sodium chloride.

3. What is the difference between dissociation and decomposition? Illustrate your answer by reference to calcium carbonate and explain why the preesnce of free carbon dioxide diminishes the extent to which the dissociation of the substance proceeds at a particular temperature.

4. Explain with illustrations :—(a) cryohydrate; (b) eutectic mixture; (c) freezing mixture; and (d) dissociation pressure.

5. What do you observe on a manometer left connected to a desiccator in which is kept a quantity of blue vitriol? Explain the observations.

6. Discuss the equilibrium between liquid and solid phase in a two component system and explain the practical application of your conclusion.

7. State and explain the phase rule and illustrate its applications to any two of the following systems :—(a) Ice—water-vapour; (b) Freezing mixture; (c) $CaCO_3 \rightleftharpoons CaO + CO_2$; (d) Sulphur and its modifications.

8. State the Phase Rule and apply it to a system of one component, comprising more than one solid phase.

PART III

ELECTROCHEMISTRY

ELECTROLYTIC DISSOCIATION & CONDUCTION—Ionic Equilibria (Dilution Law, Ionic Product of Water, Hydrolysis of Salts & Solubility Product)—Electro-Motive Force—Acids & Bases: pH & Indicators.

CHAPTER XVI

ELECTROLYTIC DISSOCIATION & CONDUCTION

Electrolytes and Non-electrolytes —If sugar is dissolved in water, such a solution does not conduct electric current whereas a solution of sodium chloride does. Substances like sugar, urea, etc., which are thus incapable of conducting electricity are called non-electrolytes.

The passage of electric current through a solution of sodium chloride, however, differs from metallic conduction in one important respect. When a current passes through a metal wire, there is no change except the heating effect, whereas on the passage of electricity through solutions of salts, etc., chemical changes also take place on the electrodes. The conductors of the latter type are known as *electrolytes* and the phenomenon of sending current through them and the accompanying chemical changes are known as *electrolysis*.
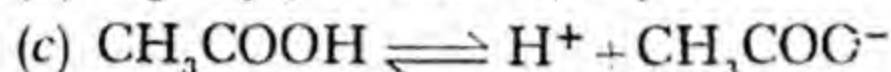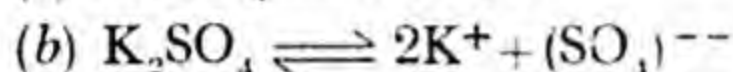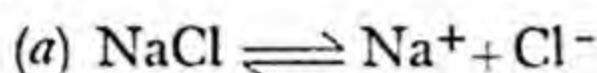
All acids, bases and salts are *electrolytes*. The presence of water is not essential since many of them are typical electrolytes even in the fused state, or in non-aqueous solution.

Though the electrolytes are fairly good conductors, they are far less conducting than pure metals. It is also found that solutions of weak organic acids and bases are very feeble conductors in comparison with those of strong acids, strong bases and salts, and so, the former are called *weak electrolytes*, as opposed to the latter, called strong electrolytes.

Electrolytic Dissociation —The mechanism of conduction of current through electrolytes was speculated upon from nearly the beginning of the last century when brisk activity was going on in the then newly discovered phenomenon of electrolysis. Of the earliest theories that of Grotthus (1806) received wide support. The original theory of Grotthus assumed the electrolyte molecules to be endowed with two poles—positive and negative,—which align themselves along the lines of force and conduct current by a '*bucket brigade*' type of mechanism.

Clausius in 1857 first conceived of the idea that solutions of electrolytes contain a very small proportion of free ions in reversible equilibrium with the undissociated molecules and these ions are responsible for conducting the current. The credit of being the originator of the *theory of electrolytic dissociation* is generally attributed to Arrhenius (1887) for the reason that he not only postulated *extensive spontaneous* dissociation of electrolytes into ions but first showed methods of calculating the *extent of ionisation* by a number of quite independent methods, which agreed fairly well amongst themselves. Arrhenius pointed out that all electrolytes deviate from van't Hoff's ideal solution equation, $P=cRT$ [(1)-XII] and the deviation is in such a way

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that there are more dissolved units than the actual number of solute molecules taken in solution. He postulated that the electrolyte molecules dissociate into ions in solution as a result of which the van't Hoff's factor, i, is always greater than unity which leads to a higher value for all colligative properties in solution. He showed the method of calculating the degree of dissociation from experimental van't Hoff's factor values (Ch. XIII, P. 204). This agreement in values was mainly responsible for the universal acceptance of the theory during its early days. According to this theory a portion of the electrolyte molecules is reversibly broken down into ions. The degree of ionisation may often be very large and it always increases with dilution approaching completeness as the dilution becomes increasingly great. The ionisation of a few substances is represented below—

(a) $NaCl \rightleftharpoons Na^+ + Cl^-$

(b) $K_2SO_4 \rightleftharpoons 2K^+ + (SO_4)^{--}$

(c) $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

(d) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$; $HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$

Strong electrolytes which conduct current more freely are to a greater extent dissociated than weak electrolytes which conduct only feebly. A decinormal solution of sodium chloride according to Arrhenius, is about 83 per cent broken down into ions while an acetic acid solution of the same strength is less than 2 per cent dissociated.

So far as *strong electrolytes* are concerned, the above concept of Arrhenius is however, of historical interest only, as it is now known that they are completely ionised at all dilutions. We shall again refer to this point later on (P. 261).

Comparision of Electrolytic Dissociation with Gaseous Dissociation—The nature and characteristics of gaseous dissociation have already been discussed (P. 41). The chief points of similarities and dissimilarities are discussed below—

Similarities :—(a) Both of them are *reversible processes*. (b) Both the processes lead to *abnormally low values* of *molecular weight*.

Dissimilarities :—(i) The products of gaseous dissociation can be separated by *mechanical means*, e.g. by diffusion, partial solution, etc. The ions cannot be so easily separated due to the strong attraction between the oppositely charged ions.

(ii) The products of gaseous dissociation are only *neutral molecules* while in the other case, they are *charged ions*. e.g.—

(a) $NH_4Cl \rightleftharpoons NH_3 + HCl$.   (b) $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

(iii) Gaseous dissociation requires no *medium* but electrolytic dissociation needs the presence of a *medium* or *solvent*.

Evidence in favour of the Theory of Electrolytic Dissociation—The theory rests upon a good deal of experimental support from various sources, the most important of which are given below :—

(a) Solid crystals, say of common salt have been shown by X-ray analysis to consist not of NaCl molecules but of Na and Cl⁻ ions, and in solution such a crystal would simply fall apart into its ions.

(b) Tubes containing solutions of metallic iodides on rapid whirling show the farthest end to be negatively charged due to the larger sedimentation rate of the large heavy iodide ion.

(c) Colour of salt solutions at high dilution is additively composed of the solvent and the two ions. Salts of the same type in dilute aqueous solution have been found to have the same type of absorption spectrum. Also $CuCl_2$ is blue in dilute solution due to Cu^{-+} ions, yellow in conc. solution due to unionised $CuCl_2$ molecules and green (i.e. a mixture of yellow and blue) at intermediate dilutions.

Fig. 87—Centrifuging of an iodide solution.

(d) The heats of naturalisation of all strong acids and bases are the same in dilute aqueous solution. (P. 121).

(e) All electrolytes have abnormally high values for osmotic pressure and related properties.

(f) Strengths of different acids calculated from their catalytic activity and other properties are in the same order as their conductivities in aqueous solutions at equivalent dilution.

(g) The theory of solubility product, Ostwald's dilution law, Kohlrausch's law, Debye-Huckel's equation and a number of other theories and laws which are directly based on the theory of electrolytic dissociation, satisfactorily explain all the phenomena in their respective fields.

Thus, the tiny speck of idea of ionic dissociation in its modified and elaborated form, has brought complete coherence in thinking and experiment in the whole realm of electrolytic solutions and so, may be said to have received general approval.

Laws of Electrolysis —As a result of his experimental researches in connection with the passage of electricity through electrolytes, Faraday (1832) discovered the relationship between the amount of chemical action occurring on the electrodes and the quantity of electricity passing. He expressed his results in the form of two laws known as **Faraday's laws of electrolysis** which may be stated as follows.—

(i) *For the same electrolyte, the amount of chemical decomposition produced at any electrode is proportional to the quantity of electricity passing.* ($w \propto Q \propto Ct$).

(ii) *If different electrolytes are included in the same circuit the amounts of substances liberated at the different electrodes are proportional to their chemical equivalents.*

Faraday's law is one of the most exact laws in physical chemistry ; it has been found to hold under varied conditions, viz. at low and high temperature, in dilute and concentrated solutions, at various pressures and in different solvents. Since the amount of decomposition is proportional to their chemical equivalents, it
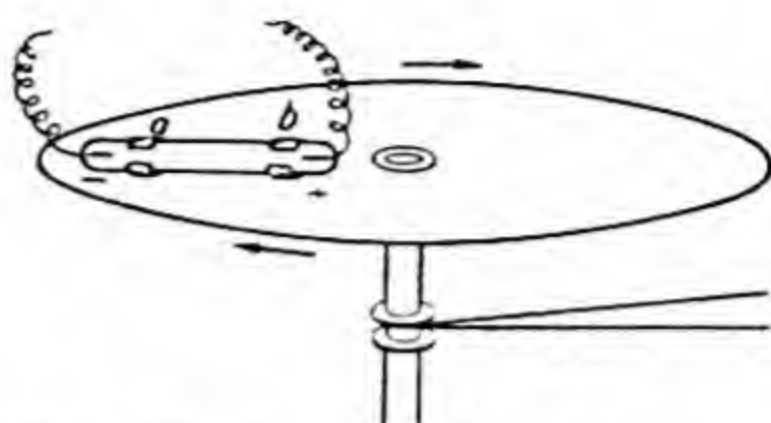
follows that the same quantity of electricity would be required to produce 1 gm equivalent of any substance, element or compound, by electrolysis. This quantity of electricity which can liberate 1 gm equivalent of any substance is called **one Faraday of electricity,** usually symbolised as **F,** and its value in practical units is 96,500 coulombs or 26·8 ampere-hours.

With our modern knowledge of electricity and matter, these laws of Faraday are seen to be a simple consequence of the fact that electricity is composed of electrons and a Faraday is simply the charge on an Avogadro number of electrons.

Electro-Chemical Equivalent—Let a quantity of electricity Q pass through an electrolyte and let w be the weight of an ion liberated at any electrode. Then according to law (i)

$w \propto Q \propto Ct$ (Since, quantity = current strength × time)

or $w = z\,Ct,$ ...   . (1)-XVI

where C is the current strength in amperes, t is the time in seconds, and z is a constant called electro-chemical equivalent.

Since $w = z$, when $Q = 1$ [i.e. $C = 1$ and $t = 1$], the electrochemical equivalent z may be defined as the quantity of a substance liberated on the passage of 1 coulomb of electricity [or, 1 ampere for 1 second]. Since the amount of decomposition is proportional to the chemical equivalent as well as to the electrochemical equivalent, we may write

$$\frac{Electro\text{-}chemical\ equivalent\ of\ A}{Electro\text{-}chemical\ equivalent\ of\ B} = \frac{Chemical\ equivalent\ of\ A}{Chemical\ equivalent\ of\ B}$$

—a relation which may be profitably used to calculate and compare the equivalents of elements.

EXAMPLE 1. *Assuming the electro-chemical equivalent of silver to be ·001118 ; find the same value for oxygen* $(Ag = 108)$.

From the relation,

$$\frac{E.\ Ch.\ Equiv.\ of\ O_2}{E.\ Ch.\ Equiv.\ of\ Ag} = \frac{Ch.\ Equiv.\ of\ O_2}{Ch.\ Equiv.\ of\ Ag} = \frac{8}{108} = ·0741$$

Or E. Ch. Equiv. of $O_2 = ·001118 \times ·0741 = ·0000828$.

EXAMPLE 2. *What weight of copper is deposited by a current of 6·2 amperes flowing for half an hour through a blue vitriol solution* (E. Ch. Eq. for $H_2 = ·0000104$; $Cu = 63·5$).

E. Ch. Eq. of Cu $(z) = $ Ch. Equiv. × E. Ch. Equiv. of H_2
$$= 31·75 \times ·0000104.$$

$\therefore$ $w = z.c.t. = (31·75 \times ·0000104) \times 6·2 \times (30 \times 60) = 3·685$ gms.

EXAMPLE 3. *A current passes through two cells containing respectively* (i) *copper sulphate solution between copper electrodes and* (ii) *silver nitrate solution between platinum electrodes. Calculate the loss or gain in weight of the different electrodes in the time in which 40 c.c. of oxygen at N.T.P. collects in the second cell.* $(Ag = 108 ; Cu = 63·5.)$

we have $\dfrac{w_1}{w_2} = \dfrac{z_1}{z_2} = \dfrac{(Ch.\ Equiv.)_1}{(Ch.\ Equiv.)_2}$, or, $w_1 = w_2 \times \dfrac{(Ch.\ Eq.)_1}{(Ch.\ Eq.)_2}$

Since 22·4 litres of oxygen weigh 1 mol i.e. 32 gms.

$\therefore$ 40 c.c. of oxygen weigh $(32 \times 40) \div 22.400 = ·0571$ gm.

∴ weight of silver deposited = ·0571 × (108/8) = 0·778 gms.

∴ weight of copper deposited = ·0571 × (31·75/8) = 0·228 gms.

∴ weight of Cu dissolved out = wt. of Cu deposited = 0·228 gms.

EXAMPLE 4. *Can you calculate mentally approximately how much current is necessary to produce oxygen gas at the rate of 1 c.c. per sec.*

One Faraday (= 26·8 amp-hour) liberates one equivalent weight = $\frac{1}{2}$ × 22·4 = 11·2 litres of oxygen gas at N.T.P. Hence at room temperature approximately 2 amps.-hours are necessary per litre of gas. Now, 1 c.c. per sec. is 3·6 litres per hours, to produce which about 3·6 × 7·2 amperes will be necessary.

The Significance of Faraday's Law —The most remarkable feature of Faraday's Law is that the amount of electrolysis depends only on the quantity of electricity passing through and so, we need not care to know the size and shape of the vessel or the electrodes, the temperature, the pressure, the voltage, or current strength or any other factor except the quantity of current and the chemical equivalent of the product. This marvel of simplicity is however quite easy to understand in the light of later knowledge. An ion, we now know, must have a charge which is a multiple of the charge of an electron, and so a chemical equivalent is associated with an N (Avogadro number) times the charge (e) of an electron and this quantity Ne is one Faraday of electricity. ($N = 6·032 \times 10^{23}$ and $e = 4·774 \times 10^{-10}$ e.s.u. = $1·60 \times 10^{-19}$ coulombs ∴ $Ne = 96,500$ coulombs = One Faraday.)

Current Efficiency —In most commercial electrolytic processes the yield of material is always less than the calculated quantity. This is not due to a breakdown of Faraday's laws but due to various side reactions or disturbances which may be taking place on the electrodes.

The ratio of the yield obtained in an electrolytic process to the theoretical yield calculated on the basis of Faraday's laws is called the *current efficiency*. In technical processes the current efficiently varies within wide limits. In the electrolytic copper refining process it is about 92 per cent while in the alkali chlorine cells it varies from 50 to 100 per cent.

Specific, Equivalent and Molar Conductivity—In the science of electricity in order to make comparison of the electrical resistance of different substances, the idea of specific resistance has been introduced. Specific resistance is defined as the electrical resistance offered between the opposite faces of a unit cube. The reciprocal of resistance is called conductivity and therefore, the reciprocal of specific resistance is called specific conductivity or specific conductance. Therefore, **the specific conductance** *is defined as the electrical conductivity between the opposite faces of a unit cube.* Throughout this book the specific conductivity will be denoted by κ, and its unit should be (see example 1) reciprocal ohms per cm, commonly called mhos (ohm read backwards) per cm.

The specific conductance of a solution is a function of the concentration ; so, to get comparable results the comparison ought

to be based on measurements on conductance in solution containing equivalent quantities of the different substances. For this purpose the idea of equivalent conductivity is largely used.

Equivalent conductance *of an electrolyte is defined as the product of the specific conductivity of the solution and the volume in c.c. which contains 1 gram equivalent of the electrolyte.* It may also be defined as the conductivity of a solution, containing 1 gm-equivalent of the electrolyte, when placed between two electrodes one centimeter apart. It is usually denoted by Λ.

Sometimes, the term, molecular conductivity (denoted by μ) is used for comparison among different electrolytes. Molecular conductivity (μ) *is defined to be equal to specific conductivity multiplied by that volume of solution in c.c., which contains one gram molecule of the electrolyte.* For salts whose equivalent weight is equal to the molecular weight, the equivalent conductivity and the molar conductivity have the same value.

EXAMPLE 5. *A decinormal solution of sodium acetate when placed between two electrodes each 1·5 cm square and placed at a distance of 0·72 cm has a resistance of 52·4 ohms. Calculate its specific conductivity.*

The relation between the dimensions of a conductor and its electrical resistance is

$$\text{Resistance} = \text{Specific resistance} \times \frac{\text{length}}{\text{area}}$$

Inserting values, we have, $52\cdot4 = \text{sp. resis.} \times \dfrac{0\cdot72}{1\cdot5 \times 1\cdot5}$

or specific resistance $= \dfrac{52\cdot4 \times 1\cdot5 \times 1\cdot5}{0\cdot72}$ ohms cm.

$\therefore$ Specific conductivity, $k = (1/\text{specific resistance}) = 0\cdot0061$ mhos/cm. Note the unit of specific resistance and specific conductivity.

If a solution is of concentration c (*i.e. c gm equivalent per litre*), then the volume in litres which contains one gram equivalent of solute is $1/c$. Therefore, volume (V) in cc containing 1 gram equivalent of solute is $= (1/c) \times 1000$. Therefore.

Equivalent conductivity, $\Lambda = \kappa V = \dfrac{\kappa \times 1000}{c}$ ... (2)-XVI

where κ is the specific conductivity of a solution of concentration, c, *i.e.* c gm. equivalent of the electrolyte per litre. This equation is very important and useful for solving numerical problems. It is to be noted that since κ is in mhos per cm and volume is in cc, the equivalent conductivity which is their product should have the unit mhos cm^2.

EXAMPLE 6. *A N/10 solution of KCl has a specific conductivity of 0·01119 mhos cm⁻¹. Find the equivalent conductivity.*

Therefore, $\Lambda = \dfrac{k \times 1000}{c} = \dfrac{\cdot01119 \times 1000}{\cdot1} = 111\cdot9$ units (mhos cm^2).

Relative Speeds of the Ions—The amounts of the cations and anions liberated at the respective electrodes are indeed in equivalent quantities, but the speeds with which the cations and

the anions travel in opposite directions are not necessarily equal. The true mechanism of conduction is made clear in the following diagram.
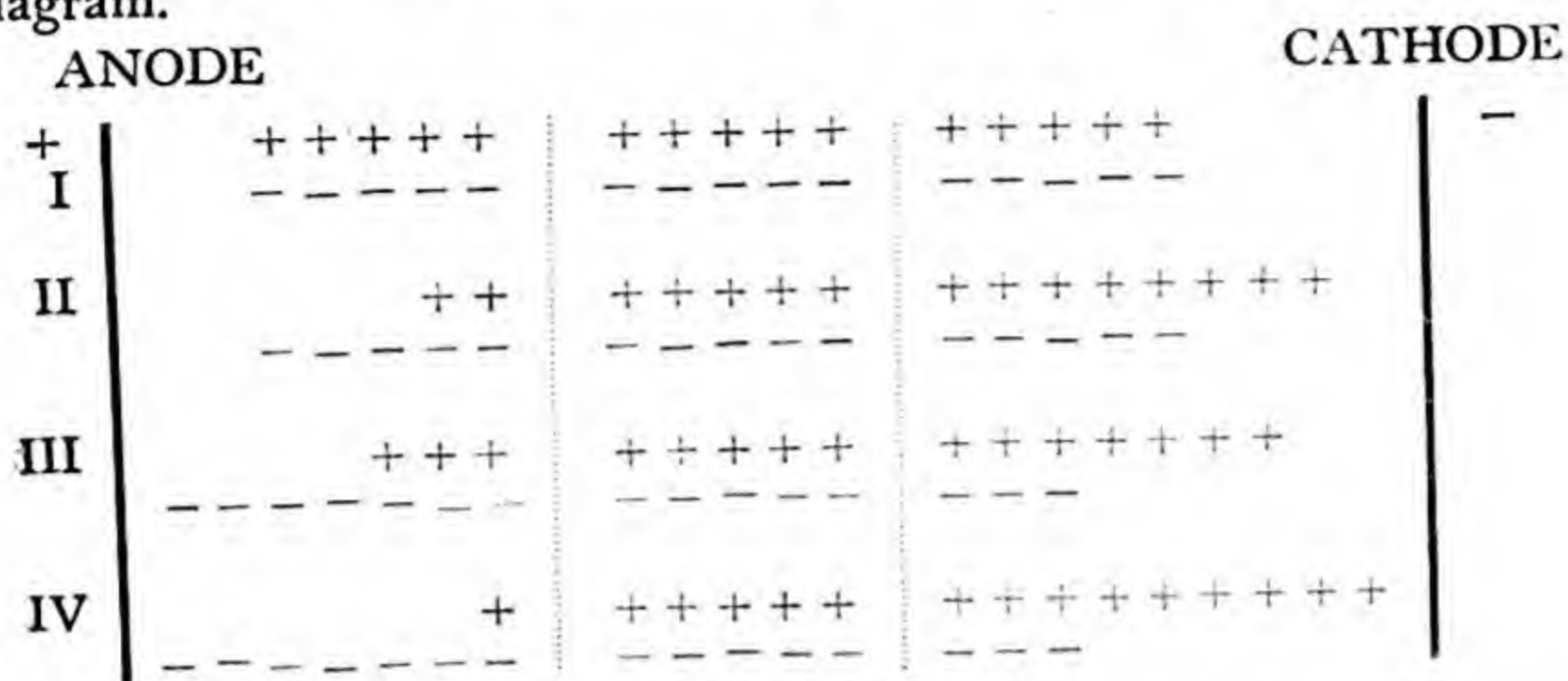
ANODE   CATHODE

Fig. 88. Migration of Ions.

In the figure, the positive ions (cations) and the negative ions (anions) are represented by (+) and (−) signs respectively. The condition before electrolysis is shown in I., an equal number of positive and negative ions being present uniformly throughout the solution. For convenience, the electrolyte is divided by two imaginary partitions represented by dotted lines into three compartments, the cathode compartment, the central compartment, and the anode compartment. Each compartment is shown to contain 5 positive and 5 negative ions, i.e. 5 complete molecules.

Suppose on establishing the electric field, only the *positive ions move* and not the negative ions, and let the current be continued for such time that each cation marches only three steps forward, i.e. three cations cross each partition. The condition is represented in Fig. 88-II. Each compartment should be electrically neutral and so, not only the *three cations* will be discharged on the cathode but also the *three anions* which are left without partners at the anode compartment will be discharged on the anode. Thus, though the anions have not migrated electrically, nevertheless, these ions have been liberated on the anode just the same. Further, *the concentration* of the electrolyte *at the cathode* compartment *has not changed* and only the anode compartment has suffered a fall in concentration.

Next *suppose* that both the ions move *at equal rate*; and then whilst, say, two anions have crossed the partition in moving towards the anode, two cations will move in the opposite direction towards the cathode. The condition will then be represented by Fig. 88-III. The point to note is that *the fall* in *concentration round each electrode is to the same extent*, and the *number of ions liberated on each electrode is the same* and is proportional to the sum of the speeds of the cation and the anion.

Now, *suppose* that the cations *move twice as fast* as the anions. Then, while two anions cross each partition in moving

towards the anode, four cations have migrated across the partitions in the opposite direction. This is represented in Fig. 88-IV. The interesting point to note is that the *number of ions* deposited at each electrode is the *same* and is proportional to the sum of speeds of the cation and the anion ; but, the *decrease in concentration round the anode is double the decrease in concentration round the cathode.*

From the above discussion we are warranted to draw the following conclusions :—

(*a*) The quantities of ion liberated at each electrode, due to electrolysis are in equivalent amount, independent of the relative speeds of the different ions, and are proportional to the sum of the speeds of the cations and the anions.

(*b*) The decrease in concentration round an electrode is proportional to the speed of the ion leaving it, *i.e.*

$$\frac{Fall\ in\ concentration\ round\ cathode}{Fall\ in\ concentration\ round\ anode} = \frac{speed\ of\ anion}{speed\ of\ cation} = \frac{v}{u} . \quad (3)$$

A further point to note is that the central portion suffers no change in concentration and the only change in concentration that takes place on electrolysis is in the vicinity of the electrodes.

Transport Numbers —We have shown in the previous section that the cations and the anions do not take equal share in carrying the electric current since they move with unequal speeds. *The fraction of the total quantity of current carried across by a particular type of ion is called* the **transport number (or Hittorf's Number)** *of that ion.* Evidently, the transport number for any ion is proportional to its speed. Therefore, if the transport numbers for the cation and the anion are n_c and n_a respectively and their speed are u and v respectively, we have

$$n_c = \frac{u}{u+v} \; ; \; n_a = \frac{v}{u+v} \; ; \; n_c + n_a = 1 \quad \ldots (4) \& (5)\text{-XVI}$$

TRANSPORT NUMBER OF CATIONS OF N/10 SOLUTION

Electrolyte	Transport number of cations, 18° C
HCl	0·835
KOH	0·265
LiCl	0·313
KCl	0·495
AgNO₃	0·471
CuSO₄	0·373
CdI₂	0·710

The values of transport number vary slightly with concentration and temperature and tend to become equal for the two ions as the temperature rises. In the table are collected some transport number values which give a fairly good idea of the *relative speeds* of the cation and the anion.

Experimental Determination of Transport Number —Transport number is determined either by *Hittorf's method* or by the *moving boundary method,* and only the former will be described here. From equations (3) and (4) it follows that a

measurement of the fall in concentration round the electrodes may serve well for the determination of transport number. But usually, in practice, the phenomenon is more complicated and allowance has to be made for secondary reactions on the electrodes.

The usual form of transport number apparatus used in the laboratory is shown in Fig. 89. The apparatus consists of a two-limbed vessel connected by a narrow straight tube. The longer tube is provided with a stop cock at the bottom for withdrawal of the solution and is usually made the anode. The electrodes are metallic in the form of a *spiral* and pass through glass tubes sealed at the mouth, just allowing the spiral portion to project out in the solution.

For the determination of the transport number of the ions of silver nitrate the electrodes are made of pure silver and the electrolyte is a standard dilute solution (less than decinormal) of silver nitrate. In series are connected a silver volta-meter, a rheostat, a battery and sometimes also a milli-ammeter. On the passage of current (10—15 milliamperes) for 2-3 hours, silver is transported from the anode compartment due to the movement of the cations (Ag^+ ions) towards cathode, but the anode itself is dissolved out by the anions (NO_3^- ions) resulting in a net increase in concentration round anode. The amount of silver dissolved out from the anode is the same as that observed to be deposited in the silver voltameter in series or is easily calculable from *Faraday's law*, $w=zct$. The difference between the increase in concentration of silver actually observed in the anode tube, A, and the amount of silver deposited in the silver voltameter is the amount of silver migrated from the anode towards the cathode. Therefore, this quantity of silver migrated divided by the total quantity of silver deposited is the *transport number* of the silver ion (*Vide* Example 8).
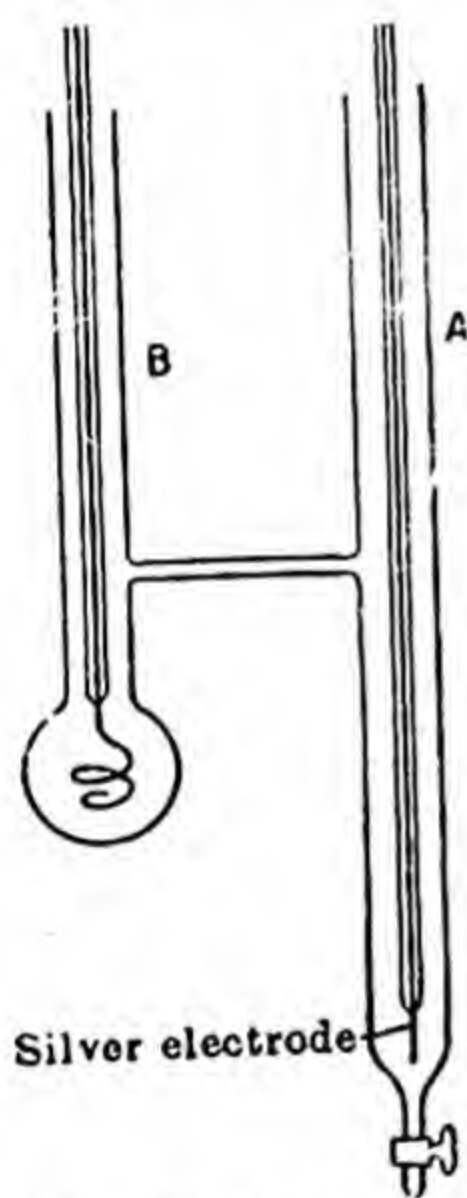
Fig. 89—Transport Number Apparatus

Silver electrode

Abnormal Values for Transport Number.—For some salts the values of transport number are abnormal in the sense that they are very high, even greater than unity for the cation and so, they are negative for the anion. In other words, the metallic part instead of migrating towards the cathode migrates towards the anode. This is ascribed to the formation of *complex ions*. In cadmium iodide, which exhibits abnormal values for transport number in concentrated solutions, it is usually assumed that the solution ionises as $2CdI_2 \rightleftharpoons Cd^{++} + [CdI_4]^{--}$ and so cadmium migrates both towards the cathode and the anode giving negative values for its transport

number. In fact, evidence from transport number determination constitutes a very definite proof for the existence of complex ions.

Experimental Determination of Conductivity—The well-known *Wheatstone's meter bridge method* is not suitable for the determination of specific resistance and specific conductivity of solutions. Because, the passage of current will be accompanied by the products of electrolysis accumulating on the electrodes which will change the effective resistance between the electrodes and will set up a counter E. M. F. Kohlrausch avoided this difficulty by using alternating current between platinised platinum electrodes so that the polarising effect of the products of electrolysis due to the current in one direction, will be neutralised by the effect of the current in the other direction. The use of alternating current will necessitate the replacement of the galvanometer by a telephone, as the latter responds to alternating current. Thus, the conditions of success are—

(a) The use of an *induction coil*, or any alternating current generator instead of a battery.

(b) The use of a *telephone*, instead of the galvanometer as current detector.

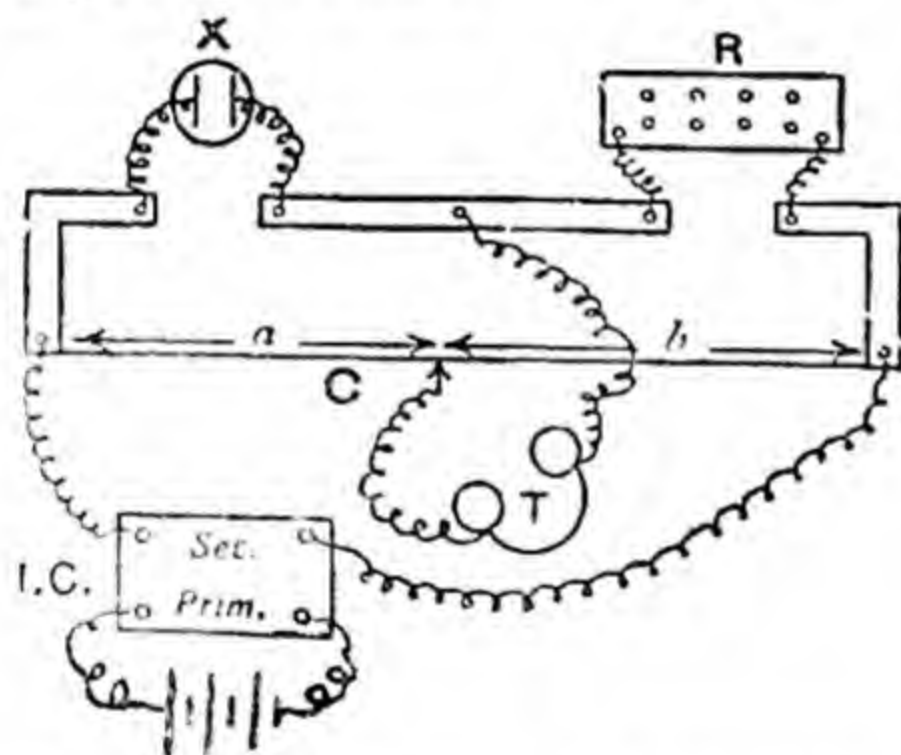(c) The electrolyte solutions should be contained in a *cell containing platinised platinum electrodes*.

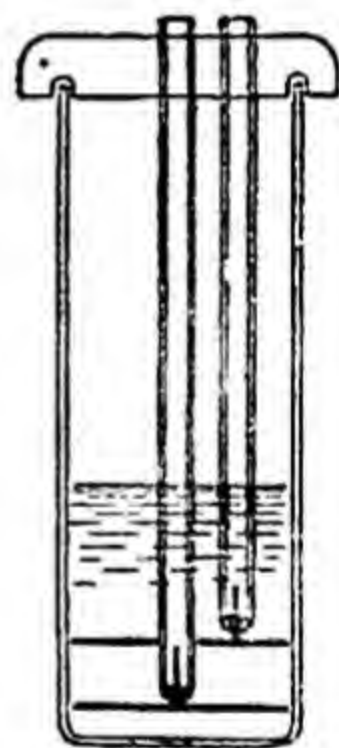Fig. 90—Determination of Conductivity of solutions

Fig. 91—Conductivity Cell

The arrangement of apparatus is shown in Fig. 90. It is an ordinary Wheatstone bridge arrangement with the modifications just referred to. The solution is contained in special cells in the gap X. while a standard variable resistance is placed in the gap R. The alternating current of usually 500—1000 cycles per sec. is obtained from an induction coil (I.C.) operated by a small battery. *ab* is a uniform platinum wire stretched along a scale graduated in millimeter. The telephone is connected to a sliding contact and the binding screw in between the solution (X) and the standard resistance (R). Sometimes, the positions of the induction coil and the telephone are interchanged. On completing the circuit, a buzzing sound is produced

in the telephone. The sliding contact is then moved along the wire until the point of minimum sound is obtained Under these

circumstances, $\dfrac{\text{resistance of the solution, } \rho}{\text{standard resistance, R}} = \dfrac{a}{b}$ ... (6)-XVI

The lengths a and b are read off the scale and the resistance of the solution, ρ is calculated from the above equation.

Since the conductivity of a solution rapidly increases with temperature, the cell should be placed in a constant temperature bath. Also, twice-distilled water (called *conductivity water*) should be used throughout.

Different forms of cells are in use ; a common form is shown in Fig. 91 which consists of a cylindrical vessel, in which two electrodes made of stout platinum foil are placed. The electrodes are of large area and are coated with platinum black, deposited on it by the electrolysis of platinic chloride solution. Connections are made by platinum wires fused through glass tubes, which are sometimes movable so that the relative distance between the electrodes may be changed.

Calculation of Specific conductivity from Experimental Data— From the observed resistance, ρ the calculation of specific resistance and *specific conductivity* could be made if the area of the electrodes and the distance between them be accurately known (*vide* Exam. 1). But the usual procedure is to calculate a factor for each cell called **cell-constant** *the product of which and the observed conductivity gives the specific conductivity.* The cell constant is known by using a solution of say, N/50 KCl, whose specific conductivity has been accurately determined by Kohlrausch and its κ value is 0·002768 mhos at 25°C.

∴ Observed Conductivity × Cell constant=Specific
Conductivity ... (7)-XVI

∴ Cell constant=Observed Resistance × Specific
Conductivity ... (8)-XVI

If the observed resistance with N/50 KCl be ρ_1, from eqn. (8) the cell constant, $K = \rho_1 \times 002768$. Therefore, if the observed resistance for any solution is ρ , (*i.e.* conductivity is $1/\rho$), the specific conductivity of the solution will be

$$\kappa = K \times \frac{1}{\rho} = K \times \frac{a}{b} \times \frac{1}{R} \qquad \qquad \text{...} \qquad \text{...} \quad (9)\text{-XVI}$$

Variation of Conductivity with Dilution —Kohlrausch determined the specific and equivalent conductivities of a number of electrolytes at various dilutions. The following table is compiled from his data.

Norma-lity	Specific Conductivity, κ			Equivalent Conductivity, Λ		
	KCl	CH_3COONa	CH_3COOH	KCl	CH_3COONa	CH_3COOH
1·0	0·0982	0·0412	0·00132	98·2	41·2	1·82
0·5	0·05115	0·0247	0·001005	102·3	49·4	2·01
0·1	0·01119	0·00611	0·00024	111·9	61·1	2·30
0·01	0·001225	0·000702	0·000143	122·5	70·2	14·3
0·001	0·0001276	0·0000752	0·000041	127·6	75·2	41·0
0·0001	0·0000129	0·00000768	0·0000107	129·5	76·8	107·0

For not too concentrated solutions, the *specific conductivity* continually *decreases with dilution.* This is due to the fact that though the total number of ions increases with dilution, owing to increased dissociation, the number of ions per c.c. decreases resulting in a diminution of specific conductivity. *The equivalent conductivity* (Λ) however continuously *increases with dilution* (Fig. 92) until it attains a *limiting value,* when on further dilution the value of equivalent conductivity does not change. This limiting value of equivalent conductivity is called the *equivalent conductance* at *infinite dilution* and is denoted by Λ_0.

Degree of Dissociation from Conductivity Data—The conductivity of a solution depends upon (*i*) the total *number of carriers* or ions, (*ii*) the *charge* or valency of the ions and (*iii*) the *speeds* of the ions. For the same electrolyte, therefore, the variation of equivalent conductivity with dilution is due to the change in the total number of ions produced by the dissociation of the electrolyte, since Arrhenius assumed that the speeds of the ions did not vary with dilution. He assumed that as the
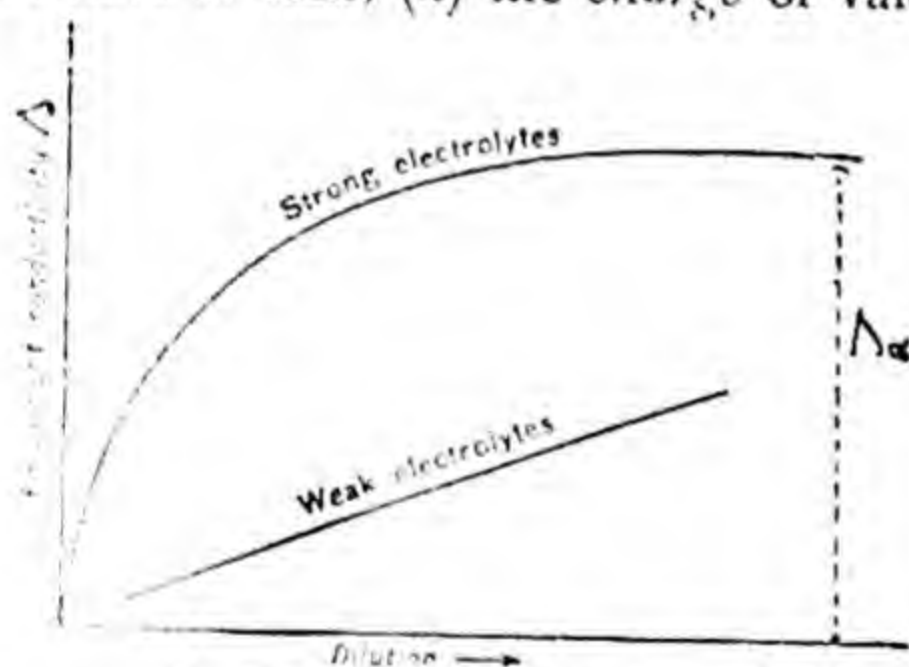

—Change of Equivalent Conductivity with Dilution

solution gets diluted, more ions are produced due to the increased dissociation of the electrolyte, until finally it gets completely dissociated into ions, when the equivalent conductivity reaches its limiting value (Λ_0) and does not further change with dilution. Since the equivalent conductance is proportional to the total number of ions, and Λ_0 signifies complete ionisation, we have,

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad \dots \qquad \dots \quad (10)\text{-}XVI$$

where α is the degree of dissociation at a dilution where Λ is the equivalent conductivity. This is a very important relation and is much used for calculating the degree of dissociation, α. (P. 204).

The validity of this calculation of the degree of dissociation, α is meaningless in the case of strong electrolytes (*vide* next section and Ch. XVII) and the value of α thus determined, is hence better called '*conductance ratio*' in such cases.

Dissociation of Strong Electrolytes —The above view of Arrhenius regarding the increase of equivalent conductivity of a strong electrolyte with dilution as due to an increase in its degree of dissociation is hardly given any credence nowadays. We now know from X-ray evidence that a strong electrolyte even in the solid crystalline state is an ordered assembly of ions without any existence of neutral molecules. This is also in accord with our idea of electrovalency. Such solids when dissolved in water or solvents having high dielectric constants would continue to remain as they were in the solid state *i.e.* would remain completely ionised. The high dielectric constant of the solvent would naturally decrease the force of attraction between the positive and the negative ions and would thus help the ions to fall apart. This would be further assisted by the solvation of the ions by the solvent.

It is hence believed that strong electrolytes are completely ionised at all dilutions. The variation of conductivity with dilution is attributed to strong interionic attraction. A positive ion is retarded in its motion by the negative ions and *vice versa*, and evidently this interionic effect decreases with dilution. Hence, the conductivity increases with dilution and attains a limiting value in sufficiently dilute solutions, when the effect of interionic attraction becomes negligible. That the interionic attraction is a powerful force to be reckoned with becomes convincingly brought home if we realise that the electrical attraction between only one gram atom of sodium ions and one gram atom of chlorine ions when separated by the maximum possible distance on the earth (*i.e.* on diametrically opposite ends of the earth) is still equal to quite a few tons weight.

The effect of interionic forces has been calculated and complicated mathematical expressions for conductivity and activity of strong electrolytes have been derived after taking into account the various factors involved. A discussion of these is beyond the scope of this book and will not be further pursued.

Kohlrausch Law—From the foregoing it is to be expected that the total current conveyed by 1 gm equivalent of an electrolyte *when completely dissociated* in a solution which is sufficiently dilute so that the effect of interionic attraction is negligible, is the sum of the amounts of current conveyed by the cations and the anions respectively independent of each other and of the dilution. Kohlrausch from his extensive experimental work also came to the same conclusion known as *Kohlrausch's law of independent migration of ions*, which may be stated as follows— *The equivalent conductivity at infinite dilution of an electrolyte is equal to the sum of the ionic mobilities of its constituent ions.*

$$\therefore \quad \Lambda_\iota = \lambda_c + \lambda_a \ldots \ldots (\textit{Kohlrausch's Law}) \qquad \ldots (11)\text{-XVI}$$

where λ_c and λ_a in the above equation exclusively refer to the cation and the anion respectively and are called *ionic conductance* or *ionic mobility*. This law of Kohlrausch is particularly useful in calculating equivalent conductance at infinite dilution (Λ_0) for weak electrolytes *e.g.*, acetic acid etc., for which a direct determination is not possible due to their low conductivity at high dilutions.
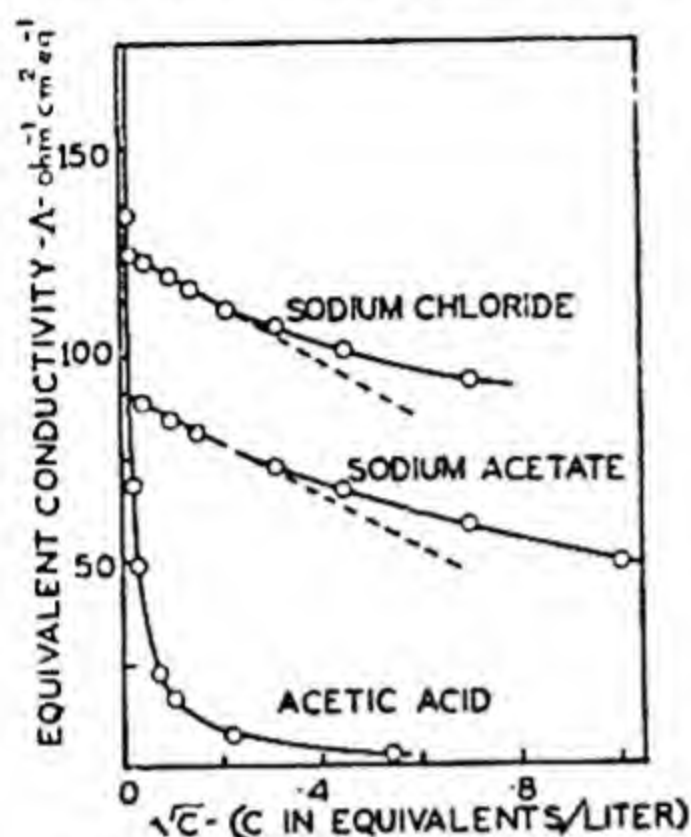

Fig. 93—Extrapolation of Λ_0

Experimental Determination of Λ_0 —The experimental determination Λ_0 depends on the property of strong electrolytes, first pointed out by Kohlrausch, that at high dilution the equivalent conductivity, Λ, when plotted against the square-root of concentration, $\sqrt{c}$ gives a straight line (Fig. 93) which meets the zero axis of concentrations at Λ_0, equivalent conductivity at infinite dilution. In other words, at high dilution, Λ_0 and c are related by the equation, $\Lambda = \Lambda_0 - k\sqrt{c}$. Λ_0 is experimentally determined by this type of extrapolation for strong electrolytes. However, Λ is not observed to attain any such limiting value with dilution for weak electrolytes as is also shown for acetic acid in Fig. 93. So, Λ_0 for weak electrolytes can not be experimentally determined but has to be computed with the help of Kohlrausch law.

Ionic Mobility, λ—The values of ionic conductances are evidently proportional to the speeds of the ions.

$$\therefore \quad \lambda_c \propto u \ : \ \lambda_a \propto v.$$

$$\therefore \quad \text{Transport number, } n_c = \frac{u}{u+v} = \frac{\lambda_c}{\lambda_c + \lambda_a} = \frac{\lambda_c}{\Lambda_0} \quad \dots \text{(12)-XVI}$$

or $\lambda_c = n_c \Lambda_0$: similarly, $\lambda_a = n_a \Lambda_0$ ... (13)-XVI

So we arrive at the very useful result that ionic mobility is merely the product of the transport number and equivalent conductivity at infinite dilution. These two equations are useful for calculation of ionic conductances (mobilities). Some typical values are collected in the following table. It may be observed that the mobilities for H^+ and OH^- ions are very high in comparison with those of the other ions.

Ion	Mobility λ_c and λ_a
H^+	318
Na^+	44·5
K^+	65
Ag^+	56
OH^-	174
Cl^-	66
Br^-	67
CH_3COO^-	34

Absolute Velocity of Ions —It is the velocity of an ion in *cm per second* when it moves under an electric field due to two electrodes placed 1 cm. apart and having a potential difference

of 1 volt between them (i.e. *under unit potential gradient*). So, the unit of absolute velocity is cm per sec per (volt/cm), *i.e.* cm² per sec per volt. The following relations have been theoretically deduced—

$$\lambda_c = U \times \mathbf{F} \; ; \; \lambda_a = V \times \mathbf{F} \qquad \qquad \ldots \; (14)\text{-XVI}$$

and so, $\quad \varLambda_0 = \mathbf{F}(U + V)$

where U and V are the absolute velocities of the cations and anions respectively, and $\mathbf{F}$ stands for one Faraday of electricity (96,500). Thus, the absolute velocities of hydrogen ion and chlorine ion are $\dfrac{318}{96,500}$ and $\dfrac{66}{96,500}$ *i.e.* 0·00329 and 0·000685 cm. per sec. per unit potential gradient. The usual speed of the common ions are of the order of 10^{-4} cm. per sec. per unit potential gradient. In other words, an ion moves about 1 cm. per hour under 1 volt per cm.

Applications of Conductivity Measurements —Since conductivity is a quantitative measure of the amount of ion present in a solution, it finds varied application in research and industry wherever electrolytes are involved. Some typical examples are discussed below :—

(*i*) **Solubility of a sparingly soluble salt**—This is determined by a direct application of equation (2) and (11). Remembering that the equivalent conductivity at such high dilution is $\varLambda_0$, according to equation (2) we have for a dilute saturated solution.

$$\varLambda_0 = \frac{\kappa \times 1000}{c} \quad \text{or} \quad c = \frac{\kappa \times 1000}{\varLambda_0}$$

where κ is specific conductivity. But $\varLambda_0$ is known from Kohlrausch's law, $\varLambda_0 = \lambda_c + \lambda_a$, λ_c and λ_a being known from Tables or separately determined from experiments with suitable salts and κ is experimentally measured and so we know c, the solubility of the salt in question.

EXAMPLE 7.—*The specific conductivity of a saturated solution of silver chloride is* $1·36 \times 10^{-6}$ *mhos. Find its solubility product, using the mobility data on P. 254.*

$$\varLambda_0 = \lambda\text{Ag} + \lambda\text{Cl} = 56 + 66 = 122$$

But $\varLambda_0 = \kappa \times 1000/c$ or $122 = 1·36 \times 10^{-6} \times 1000/c$

∴ Solubility of AgCl, $c = 1·36 \times 10^{-6} \times 1000/122 = 1·11 \times 10^{-5}$

∴ Solubility Product (*vide* Ch. XVII) $= c^2 = 1·23 \times 10^{-10}$

(*ii*) **Conductometric Titrations**—If an acid is titrated with a base, the fast moving H^+ ions get replaced by the cation of the base. For example, on titrating HCl with NaOH, the H^+ ions, which have extraordinarily high mobility, are progressibly replaced by the much slower Na^+ ions in course of the titration.

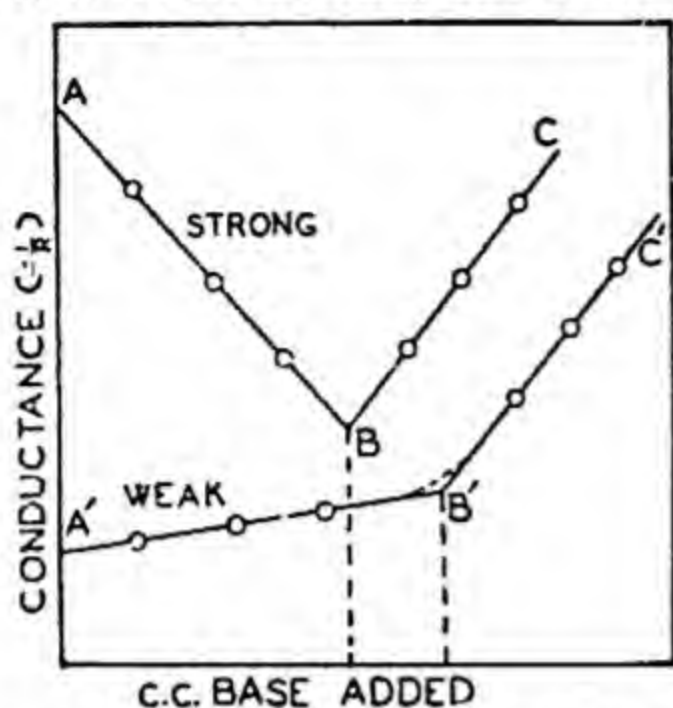As a result of this, the conductivity of the solution decreases, and attains a minimum value at the neutralisation point. Beyond the equivalence point the conductivity again increases as more electrolyte is now added to the system. So, if we plot the conductivity of the solution in any arbitrary unit against the volume of alkali added, the curve would look like two straight lines meeting at the equivalence point as shown in Fig. 94. This behaviour can be used for locating the end point in volumetric analysis for, we may determine the conductivity of a few solutions before and also beyond the equivalence point, and draw two intersecting straight lines as shown in Fig. 94. The volume corresponding to the point of intersection gives the equivalence point.

Fig. 94—Conductivity Titration

This method can also be applied for titrating weak acids or bases (Fig. 94) as also for finding the equivalence point in precipitation reactions. The location of end point by electrical method is called *electrometric titration* and so, conductometric titration is a type of electrometric titration.

(*iii*) **Other Applications**—Among other applications are the determination of hydrolysis of salts of a weak base (*vide* Ch. XVII, P. 272), the determination of the rate of a reaction involving at least one electrolyte (for example, hydrolysis of acetic anhydride), the determination of the ionisation constant of water (*vide* Ch. XVII. P. 263), control of the purity of water and of various industrial processes, etc., for details of which the student is referred to a more advanced text-book.

EXAMPLE 8. *In a transport number experiment, a solution of silver nitrate containing 0·0074 gms. per gm. of water was used. During the experiment 0·0785 gm. of silver was deposited in a silver voltameter placed in series with the transport apparatus. After the expt. 25 gms. of the anode solution contained 0·2553 gm. of silver nitrate. Find the transport number of silver and nitrate ions. The electrodes are of silver.*

Before expt. 25 gms. of water contained $0·0074 \times 25 = 0·185$ gm. of silver nitrate. After expt. 25 gms. of soln contained 0·2553 gm. of nitrate.

∴ Increase in silver nitrate at anode = 0·0703 gm. = 0·0446 gm. of Ag. But 0·0785 gm. of silver has dissolved from the anode; therefore the amount of silver transported from the anode compartment = 0·0785—0·0445 = 0·0339 gm.

∴ Transport number of silver ion = $0·0339 \div ·0785 = ·432 = 43·2\%$

Transport number of nitrate ion = $1—·432 = ·568 = 56·8\%$.

EXAMPLE 9. *The conductivity of a decinormal solution of sodium chloride is 0·00918. The ionic conductances of sodium and chlorine ions at*

the same temp. are 43·2 and 65·3 respectively. Calculate the degree of dissociation (conductance ratio) at this temp.

$$\Lambda = \frac{\kappa \times 1000}{c} = \frac{·00918 \times 1000}{·1} = 91·8$$

$$\Lambda_0 = \lambda c + \lambda a = 43·2 + 65·3 = 108·5$$

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{91·8}{108·5} = 0·846 \text{ or } 84·6 \text{ per cent}$$

EXAMPLE 9. *The molecular conductivity of a solution of silver nitrate at infinite dilution at 18°C is 115·8 The transport number for nitrate ion in silver nitrate is 0·53. Find out the velocity of silver ion for a potential drop of 10 volts per cm.*

$$\lambda_c = \Lambda_0 \times n_c = \Lambda_0 \times (1 - n_a) = 115·8 \times 0·47.$$

$$u = \lambda_c/F = (115·8 \times 0·47)/96,500 = 0·000564 \text{ cm./sec. per unit pot. grad.}$$

Velocity for 10 potential gradient $= 10 \times u = 0·00564$ cm./sec.

EXERCISES

1. State the laws of electrolysis. The same current is passed through acidulated water and a solution of stannous chloride. What volume of detonating gas (mixture of hydrogen and oxygen) measured dry at 0°C and 760 mm pressure is evolved from the water when one gram of tin is deposited from the other solution (Sn=119.) [0·282 litres]

2. Calculate the volume of electrolytic gas evolved (at N. T. P.) and wt. of copper deposited when a current of 1 ampere is passed for forty-five minutes through a voltameter containing acidulated water and one containing copper sulphate solution containing copper electrodes.
[0·472 litres; 0·885 gm.]

3. State Faraday's laws of electrolysis. A current passes through solutions of (a) silver nitrate, (b) copper sulphate and (c) acidulated water. What amounts of silver and copper will be deposited in (a) and (b) respectively in the time 300 c. c. of hydrogen at N. T. P. collect in (c)? (Ag = 108; Cu = 63). [2·893 gms; 0·8437 gms]

4. What is meant by the transport number of an ion? How is it determined? A molar solution of CdI_2 showed an anion transport number of 1·12. How would you account for the result?

5. An aqueous solution of copper sulphate is electrolysed between copper electrodes until 0·2294 gram of copper is deposited. Before electrolysis the solution at the anode contained 1·1950 gms. of copper and after electrolysis 1·34 grams. Calculate the transport number for copper and sulphate ion. [0·368; 0·632]

6. Give a short account of the theory of electrolytic dissociation and indicate what explanation it gives of (a) electrolysis and (b) the heat of neutralisation of a strong acid by a strong base.

7. How does ordinary dissociation differ from electrolytic dissociation?

8. What are the products of electrolysis when the following are electrolysed and why? (i) Fused sodium chloride between carbon poles (ii) Sodium chloride solutions between carbon poles, (iii) Copper sulphate solution between (a) carbon poles and (b) copper poles, (iv) Silver nitrate solution between (a) platinum poles, and (b) silver forming positive and copper forming negative pole.

9. Give a brief account of the Arrhenius theory of electrolytic dissociation, and show that it provides an explanation for the abnormal osmotic pressure observed in the case of electrolytes.

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10. State how you would proceed to determine experimentally the specific conductivity of a solution of acetic acid.

11. Write short notes on :—(a) Transport number (b) molecular conductivity (c) Kohlrausch's law and (d) specific conductivity.

12. At 25°C the specific conductivity of butyric acid at a dilution of 64 litres (i.e. 1 mol. in 64 litres) is 1.812×10^{-4} r.o. The equiv-conductivity at infinite dilution is 380. What is the degree of dissociation, the concentration of hydrogen ions in the solution and the dissociation constant of the acid.

$$[a = 3.05\%, \ [H+] = 4.77 \times 10^{-4}[N]; \ 1.422 \times 10^{-5}]$$

13. Find out the velocity of K+ ion in aqueous solution at 18°C under a potential gradient of 6 volt per cm. from the following data :— $_{1.}$ for KCl at 10°C = 130. Transport number of Cl⁻ in KCl = 0.495. [0.004 cm/sec.]

14. The specific conductivity of a 0.1 molar solution of a 1-1 salt is 0.00920. Calculate the equivalent conductance and the amount of dissociation, given that the equivalent conductance is 108.9 at infinite dilution.   [92.0 ; 84.5 per cent]

15. The Ostwald dilution law constant for ammonia solutions is 17×10^{-6} Calculate the amount of dissociation in a 0.1 M solution of ammonia. $[1.304 \times 10^{-2}]$

16. Calculate the degree of electrolytic dissociation of monobromacetic acid from the following data :

V in litre	...	32	128	∞
λ_v	...	73.2	130.4	385.9

What is the affinity constant of the acid?

$$[18.9\%, 33.7\% : 1.39, 1.35 \times 10^{-3}]$$

17. Explain what is meant by equivalent conductivity of an electrolyte. Describe the method you would adopt to measure this quantity, as also the value at infinite dilution.

18. Is it possible to determine the $_{1.}$ equivalent conductivity at infinite dilution for hydrochloric acid and acetic acid by the same experimental procedure? Discuss thoroughly the principles involved.

19. Acetic acid and ammonia have the same value for their ionisation constants at a given temperature. If the pH of a solution of acetic acid is 3, what is the pH of an ammonia solution of equal molar strength. $[pK\omega - 3]$

20. What is the unit for the following :—(a) specific conductivity, (b) equivalent conductivity (c) transport number (d) cell constant and (e) dissociation constant.

21. Conductivity water has a specific conductivity of 10^{-6} mhos cm⁻¹. If an ohmmeter can measure in the range 50 to 1000 ohms, what should be the cell constant and dimensions of the cell electrodes to be used for the purpose. [Cell-constant (or interelectrode distance/area of electrode) in the range 1 to 2×10^{-4}].

22. Prove that the cell constant is approximately equal to the distance between the two electrodes divided by the mean area of the electrodes.

CHAPTER XVII

IONIC EQUILIBRIUM

Ostwald's Dilution Law—Ionisation of Water—Hydrolysis—Solubility Product

General—If a binary electrolyte BA is dissolved in water, a portion of it breaks down into ions B^+ and A^-, which are in equilibrium with the undissociated molecules, BA.

$$BA \Longleftrightarrow B^+ + A^-$$

$$e.g. \quad CH_3COOH \Longleftrightarrow H^+ + CH_3COO^-$$
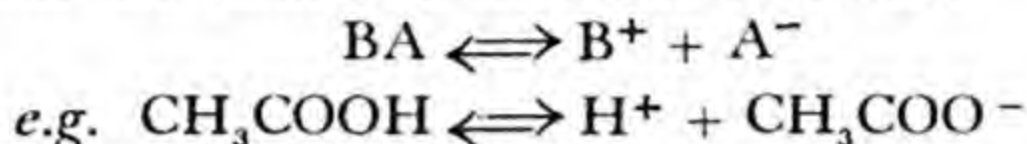
The fraction of the total number of molecules present as ions is known as the degree of dissociation of the electrolyte. The degree of dissociation will depend on dilution and as a general rule *the more dilute the solution the greater is the degree of dissociation.*

N.B. The reason for increased dissociation on dilution is that the forward reaction is directly proportional to the concentration of BA (unimolecular) while the reverse reaction is proportional to the product of concentrations of B^+ and A^- (bimolecular). So, on diluting to say, double volume, the speed of the direct reaction falls to half but that of the reverse reaction falls to one-fourth only, and so, the reaction goes towards the forward direction and the equilibrium gets displaced to the right.

Ostwald's Dilution Law —Suppose that originally one gram-molecule of a binary electrolyte, say, acetic acid, is dissolved in 'v' litres of water and that at equilibrium a fraction 'α' of it is dissociated into ions.
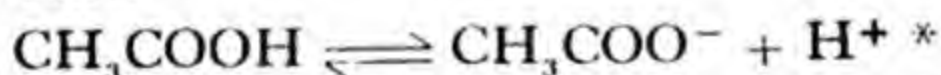
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \text{ *}$$

Then, as a result of ionisation, 'α' mols of CH_3COO^- and α mols of H^+ and $1 - \alpha$ mols of undissociated acid will be present.

Applying the law of mass action, we get,

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]} = \frac{\alpha^2}{(1-\alpha)v} = \frac{\alpha^2 c}{(1-\alpha)} \qquad \ldots (1)\text{-XVII}$$

where K_a is the ionisation constant or the **dissociation constant** of the acid. Note that K_a has the dimension of concentration. and like any other equilibrium constant, is a constant only at a constant temperature. This equation representing the variation of the degree of dissociation with dilution is known as **Ostwald's dilution law** and is an extremely important relation in the realm of electrochemistry of solutions and should be memorised.

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* The hydrogen ion. H^+ is present in water as the hydronium ion. H_3O^+ ($H^+ + H_2O$). However, for the sake of simplicity we shall throughout use the symbol, H^+ for hydrogen ion, solvated or unsolvated, remembering that the hydrated ion is present in water.

Since the degree of dissociation, x is generally determined by conductivity measurements, the above formula can be put in a different form by substituting Λ/Λ_0 for x (eqn. 10-XVI).

It then becomes
$$\frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)} = K_a \qquad \ldots \qquad \ldots \quad (2)\text{-XVII}$$

The dilution law was tested by Ostwald and others by conductivity measurements and was found to hold good fairly well for weak acids and bases. The following table compiled for acetic acid shows the constancy of the *dissociation constant*, K.

Dilution v (*litres*)	Degree of Dissociation x (*per cent*)	Dissociation constant $K_a \times 10^5$
0·994	0·40	1·62
2·02	1·614	1·88
15·9	1·66	1·76
18·1	1·78	1·78
1500·0	14·7	1·69
7480·0	30·1	1·72

It would be seen that the value of K_a for acetic acid remains fairly constant for a wide range of concentration. It is of interest to note that the acid is dissociated to a very small extent under ordinary concentration : a normal solution is dissociated to only 0·40 per cent and even a thousandth normal solution is dissociated to only 12 per cent.

If the degree of dissociation is very small, as is usually the case for weak electrolytes at ordinary concentrations, $(1 - x)$ is almost equal to unity and so the dilution law becomes

$$\frac{x^2}{v} = K \text{ or, } x = \sqrt{Kv} = \sqrt{\frac{K}{c}} \qquad \ldots \qquad \ldots \quad (3)\text{-XVII}$$

that is, for weak electrolytes *the degree of dissociation is inversely proportional to the square root of concentration.* The above equation can be interpreted in other ways. It directly follows that *for two weak acids the degrees of dissociation are directly proportional to 'he square root of their dissociation constants.* Thus if $c = 1$, $x = \sqrt{K}$ or in other words, *the degree of dissociation of a normal solution of a weak electrolyte is approximately equal to the square root of its ionisation constant.* If x is not negligible in comparison with unity, the equation becomes a quadratic one with respect to x and on solving gives

$$x = -\frac{Kv}{2} + \sqrt{Kv + \frac{K^2 v^2}{4}} \qquad \ldots \qquad \ldots \quad (4)\text{-XVII}$$

The physical significance of the dissociation constant K can

be derived by substituting the value $\alpha=\frac{1}{2}$ in the dilution law;

$$\therefore \quad K = \frac{(0.5)^2 c}{0.5} \quad \text{or,} \quad K = \frac{c}{2} \quad \text{or,} \quad c = 2K$$

In other words, *the concentration at which the electrolyte is half-dissociated is twice the value of the dissociation constant.* For acetic acid, K_a is 0·000018 ; therefore, at a concentration equal 0·000036 N (1 gm mol dissolved in 13,850 litres approx.) acetic acid will be fifty per cent dissociated.

EXAMPLE 1. *The specific conductivity of a 0·5% solution of acetic acid is 0·0004525 cm.$^{-1}$ ohm^{-1} at 18°C. Calculate its dissociation constant.*

$c = (5/58)$ mol./litre, $\alpha = \Lambda/\Lambda_0$. But $\Lambda = k \times 1000/c = 5.25$ and
$\Lambda_0 = \lambda_{H^+} + \lambda_{CH_3COO^-} = 318 + 34$ (P. 254). $= 352$.

$$\therefore \quad \alpha = ·0149 \qquad \therefore \quad K_a = \frac{\alpha^2 c}{1-\alpha} = 1·942 \times 10^{-5}.$$

EXAMPLE 2. *A deci-normal solution of acetic acid is ionised to the extent of 1·3 per cent. Find the ionisation constant of acetic acid.*

$[H^+] = 0·1N \times 0·013 = 1·3 \times 10^{-3}$ N
$[CH_3COO^-] = H^+ = 1·3 \times 10^{-3}$ N

Undissociated acid, $[CH_3COOH] = $ total—dissociated portion
$= (1-\alpha)c = (1-0·013)c = 0·987 \times 0·1$

$$\therefore \quad K = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(1·3 \times 10^{-3})^2}{0·987 \times 0·1} = 1·71 \times 10^{-5}$$

Validity of the Dilution Law —The dilution law holds good only for weak electrolytes, viz. organic acids and bases, but *does not hold for strong electrolytes* because, the latter are completely dissociated at all dilutions, and the conductance ratio does not

Dilution (v litres)	$\alpha = \dfrac{\Lambda}{\Lambda_0}$	$K = \dfrac{\alpha^2}{(1-\alpha)v}$
1	0·756	2·350
5	0·831	0·815
50	0·923	0·824
1000	0·980	0·048

represent their degree of ionisation (*vide*, Ch. XVI, P. 253). Thus, it applies in the case of acetic acid but not for sodium acetate, which latter is a strong electrolyte. The foregoing table for potassium chloride shows clearly that the dissociation constant, K calculated on the basis of the dilution law and conductance ratio shows a great variation for strong electrolytes.

The explanation of this anomaly was given by Milner (1912), Ghosh (1918) and by Debye and Hückel (1923), on the basis of complete dissociation, discussions of which are well beyond the scope of the present book.

Equilibrium between Electrolytes in Solution : Effect of Common Ion —If two electrolytic solutions are mixed the degree

of dissociation of each is usually changed. This change in concentration may be large if they contain an ion in common. The interesting case is that of a weak acid or base in presence of ions of its salts.

For example, if to a solution of acetic acid some sodium acetate is added, the equilibrium will change. Acetic acid ionises giving H^+ and CH_3COO^- ions and there is established the equilibrium, $[H^+] \times [CH_3COO^-] = K_a \times [CH_3COOH]$. The introduction of sodium acetate which is almost completely ionised increases the concentration of acetate ion and since the concentration of unionised acetic acid can not increase very much, as the dissociation is usually small, the concentration of $[H^+]$ ion should proportionately decrease to maintain the same value of the equilibrium constant. Therefore, we may propound the rule that *the introduction of a salt with a common ion decreases the degree of dissociation of a weak electrolyte.* The exact relationship can easily be derived on the basis of the dilution law, when it can be shown that if the added substance is a strong electrolyte and the substance, whose degree of dissociation is considered, is a weak electrolyte, the degree of dissociation is approximately *inversely* proportional to the concentration of the added substance, the proof of which is left to the student as an exercise.

Isohydric Solution—If on mixing together two electrolytic solutions having a common ion there is no change of the degree of dissociation of any of them, such solutions are called *isohydric solutions.* The relative concentration at which two solutions, say, two acids become isohydric can be easily calculated. Let us suppose that two solutions containing respectively the acids HA_1 and HA_2 be isohydric. Let v_1 and v_2 be the original volumes of the two solutions and a_1 and a_2 be their respective degrees of dissociation. On mixing, the total volume becomes $v_1 + v_2$ and the hydrogen ion concentration $(a_1 + a_2)/(v_1 + v_2)$. Applying Ostwald's dilution law to the original solution we get,

$$\frac{a_1^2}{(1-a_1)v_1} = K_1 \dots (a) \qquad \frac{a_2^2}{(1-a_2)v_2} = K_2 \dots (b)$$

Applying the dilution law to HA_1 in the mixed solution, we have

$$\frac{(a_1+a_2)a_1}{(1-a_1)(v_1+v_2)} = K_1 \dots (c)$$

Dividing eqn. (c) by eqn. (a), we have

$$\frac{(a_1+a_2)v_1}{(v_1+v_2)a_1} = 1 \quad \text{or} \quad \frac{a_1}{v_1} = \frac{a_2}{v_2} \quad \text{or} \quad [H^+]_1 = [H^+]_2$$

Therefore, *the condition of isohydricity is that the common ion should have the same concentration in both the solutions before mixing* and it depends in no way on the total volumes of the solutions mixed.

Ionisation of Water—Even the purest water is not an absolute non-conductor but conducts current very feebly suffering electrolysis. This weak electrolytic behaviour of water is due to the presence of very small quantities of hydrogen (H^+) and hydroxyl (OH^-) ions, which are in equilibrium with undissociated water molecules according to the equation,

$$H_2O \rightleftharpoons H^+ + OH^-$$
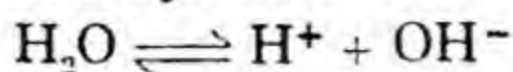
or more correctly, $2H_2O \rightleftharpoons H_3O^+ + OH^-$

Applying the law of mass-action,

$$K = \frac{[H^+][OH^-]}{[H_2O]} \qquad \ldots \qquad \ldots \qquad \ldots \quad (5)\text{-XVII}$$

Since in water the active mass of H_2O is constant, we have

$$[H^+] \times [OH^-] = K[H_2O] = K_w \quad \text{(constant.)} \qquad \ldots \quad (6)\text{-XVII}$$

where K_w is called the **ionic product** for water. In pure water $[H^+]=[OH^-]$; $\therefore$ $K_w=[H^+]^2=[OH^-]^2$. The value of ionic product is independent of whether the solution is acidic or alkaline and has got the same value in all solutions [also *vide* Ch. XIX].

It may make things clear for beginners to be pointed out that K_w is the ionic product of water but not the dissociation constant of water which is K in eqn. (5) and its value is $1/55\cdot5$ times that of K_w since $[H_2O]=$ number of mols of water in one litre $= 1000/18 = 55\cdot5$.

Evidences for Ionisation of Water —The direct proof of the presence of ions in water lies in the fact that even the purest water has got a small but definite *electrical conductivity*. That the ions are $[H^+]$ and $[OH^-]$ is proved by the capacity of water to catalyse, though to a small extent, all reactions catalysed by acids and bases, and from a measurement of this *catalytic power* of water an approximate estimate of its hydrogen and hydroxyl ion concentrations can be made. Another definite indication lies in the phenomenon of *hydrolysis* of salts (*see later*), which can only be explained by the presence of weak acidic and basic power of water. At room temperature $(25°C)$ the hydrogen ion concentration of pure water has been experimentally found to be about 10^{-7} *gm. ion per litre, i.e.* in 10 million litres of water there is one gram of hydrogen ion. Therefore, at $25°C$ the value for the above constant, $K_w = (10^{-7})^2 = 1 \times 10^{-14}$.

EXAMPLE 3. *Sp. conductivity of pure water at $25°C$ is 0.58×10^{-7} r.u. Calculate K_w, the ionic product of water.*

Since $55\cdot5$ mols of water are present in a litre,

$$\Lambda = k \times 1000/c = 0.58 \times 10^{-7} \times 1000/55\cdot5$$

$$\Lambda_0 = \lambda_{H^+} + \lambda_{OH^-} = 350 + 198 = 548$$

$$\therefore \quad \alpha = \Lambda/\Lambda_0 = 1.9 \times 10^{-9}$$

$$\therefore \quad [H^+] = [OH^-] = \alpha c = 1.9 \times 10^{-9} \times 55\cdot5 = 1.05 \times 10^{-7}$$

Hence, $K_w = [H^+][OH^-] = (\alpha c)^2 = 1.10 \times 10^{-14}$

Ionisation of Double Salts and Complex Salts—Though both double salts and complex salts have got an individuality of their own in the solid state, they behave quite differently in solution with respect to their mode of ionisation. The double salts behave in solution as just a mixture of its constituent salts whereas complex salts contain new ions as is illustrated by their ionisation below.

Double salts :—Mohr's salt, $FeSO_4$, $(NH_4)_2SO_4,6H_2O$; Alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$; Carnallite, KCl, $MgCl_2$, $6H_2O$; etc.

$$FeSO_4,(NH_4)_2SO_4,6H_2O \rightleftharpoons Fe^{++} + 2SO_4^{++} + 2NH_4^+$$
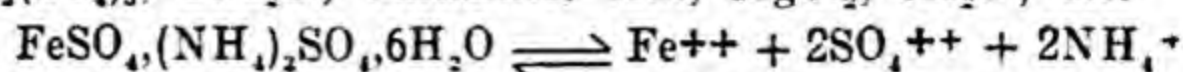
Complex salts :—Potassium Ferrocyanide, $K_4Fe(CN)_6$; Nessler's compound, $KHgI_3$. etc.

$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + Fe(CN)_6^{----}$$
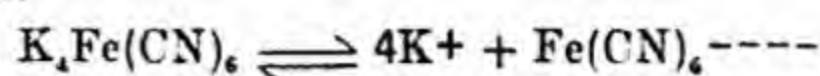
Hence, the distinction between a double salt and a complex salt reduces to a difference in the degree of ionisation of the complex ion. If the complex ion is very stable and ionises very little it is a typical complex salt and if the complex ion is too unstable to exist at all and ionises completely it is a double salt. The stability of complex ions is so strong that potassium silver cyanide $[KAg(CN)_2]$ is actually injected into the human body for the prophylactic effect of silver salts and has none of the poisonous effects of the cyanides.

It is however, possible to obtain salts where the stability of the complex ion is intermediate between these two extremes. Thus, $K_2Cd(CN)_4$ contains sufficient Cd^{++} ions as well as the complex $(Cd(CN_4)^{--}$ ions. *So the distinction between complex and double salts is not a sharp one* and salts of all intermediate degrees of complexity exist. In other words, *the double salts and complex salts differ in degree but not in kind.*

Sequestration of Ions—Heavy metal ions, which are usually precipitated out by reaction with anions, can be held in solution by complex formation with suitable substances. This sort of masking of ions is known as *sequestration* and the complex-forming substances as *sequestering agents*. The most powerful sequestering agents, so far discovered, are sodium salt of ethylene diamine tetraacetic acid, $[(CH_2COOH)_2N - CH_2 - CH_2 - N(CH_2COOH)_2]$ and some polyphosphates. The sequestering effect of EDTA is so pronounced that it can even prevent the precipitation of $BaSO_4$, $CaCO_3$, etc. Consequently, these are extensively used in industry nowadays, wherever harmful heavy metal ions are present, e.g., in water softening, water treatment, fountain pen ink manufacture, etc. Based on this peculiar property of EDTA, direct titration of heavy metals by EDTA, called complexometric titration has been developed and used for rapid and accurate determination of say, hardness of water. The most likely mechanism of sequestration of E.D.T.A. is formation of a polydentate complex through the two nitrogen atoms with the heavy metal ion :—

$$
\begin{array}{ccc}
^-OOCH_2C & & CH_2COO^- \\
| & & | \\
H_2C-N & \rule{1cm}{0.4pt} & N-CH_2 \\
| & \searrow \quad \swarrow & | \\
& Ca & \\
OC-O & \diagup \quad \diagdown & O-CO
\end{array}
$$
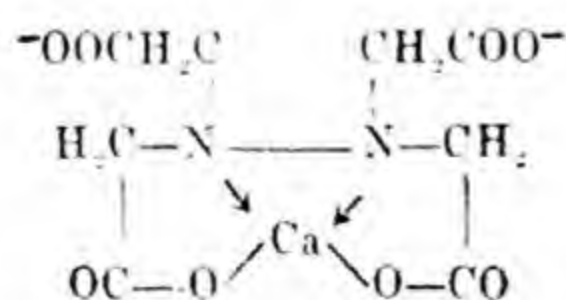
Equilibrium of Polyhalide Formation—Bromine and iodine molecules owing to their high electric polarisability have the

peculiar property of combining with halide ions to form trihalide ions, X_3^-, giving rise to the following types of ionic equilibria.

$$I^- + I_2 \rightleftharpoons I_3^- ; \quad Br^- + Br_2 \rightleftharpoons Br_3^- ; \quad I^- + Br_2 \rightleftharpoons IBr_2^- ; \quad \text{etc.} \quad (1)$$
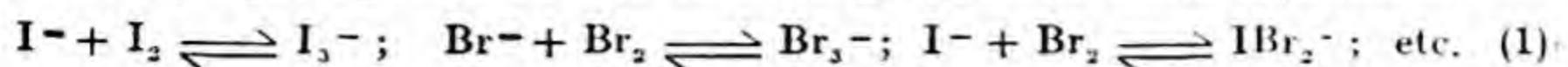
Therefore, if iodine is added to a solution of KI it dissolves to form the unstable complex ion I_3^- according to equilibrium (1). Alternatively, we may consider a trihalide ion to be a weak electrolyte dissociating into a halogen molecule and a halide ion $(I_3^- \rightleftharpoons I_2 + I^-)$ and obeying the Ostwald dilution law. The equilibrium constant of this and similar reactions can be easily determined by partition experiments using immiscible solvents. Thus, if the above system is shaken with $CHCl_3$, the concentration of free iodine in the aq. layer is known by applying Nernst distribution equation (P. 170) from that in the non-aqueous layer obtained by analysis. All other substances present are insoluble in $CHCl_3$, and so starting with known amounts of KI and I_2 we can calculate the concentrations of all the three ions, and hence, the equilibrium constant. An example shown below makes the method of calculation clear.

EXAMPLE 4. *At 13·5°C I_2 was distributed between an aq. solution of KI and CS_2. Calculate the equilibrium constant of the reaction $KI + I_2 \rightleftharpoons KI_3$, in the aqueous layer, from the following data :— Total conc. of I_2 in the aq. layer = 0·02832 mols/litre ; total conc. of KI in the aq. layer = 0·125 mols/litre ; conc. of I_2 in CS_2 layer = 0·1896 mols/litre ; partition co-efficient $k = CS_2/H_2O = 625$.*

The equilibrium constant, $K = \dfrac{[I_3]}{[KI][I_2]}$, the squared brackets indicating conc. in the aq. layer.

Now, conc. of free I_2 in H_2O, i.e., $[I_2]_{aq} = \dfrac{0\cdot1896}{625} = 3\cdot034 \times 10^{-4}$

$[I_3^-]$ = Total conc. of I_2 in H_2O—Conc. of free I_2 in H_2O
$= 0\cdot02832 - 3\cdot034 \times 10^{-4} = 28\cdot02 \times 10^{-3}$

$[I^-]$ = Total conc. of KI in water—Conc. of KI_3
$= 0\cdot125 - 28\cdot02 \times 10^{-3} = 96\cdot98 \times 10^{-3}$

$\therefore \quad K = \dfrac{28\cdot02 \times 10^{-3}}{3\cdot034 \times 10^{-4} \times 96\cdot98 \times 10^{-3}} = 95\cdot22 \times 10^{2}$

Hydrolysis of Salts—Aqueous solutions of neutral salts are not necessarily neutral in reaction and very often they are acidic or alkaline in reaction. Thus, a solution of potassium cyanide is strongly alkaline to litmus. The process which takes place is the reaction of the salt with water liberating the free acid and the free base of the salt, which makes the solution acidic or alkaline depending upon the relative strengths of the acid and the base thus liberated. This process of *decomposition of a salt by water is called hydrolysis.*

The hydrolysis of a salt BA, may be expressed in its simplest form as follows—

$$BA + H_2O \rightleftharpoons BOH + HA$$
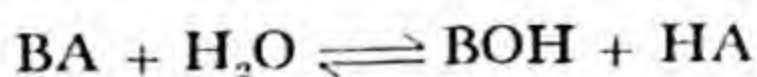
If the base BOH be stronger than the acid HA, the solution would contain an excess of OH⁻ ions and therefore, would react alkaline ; on the other hand, if the acid HA be stronger than the base B(OH), there would be an excess of H⁺ ions and the solution would react acidic. If the base and the acid are of equal strength, the concentrations of H⁺ and OH⁻ ions would be equal as in pure water and so, the solution would be neutral.

The matter may be looked upon from a slightly different view-point. As shown previously, water contains a small concentration of H⁺ and OH⁻ ions and hence, it may be regarded both as a weak acid and as a weak base. So, when a salt is dissolved in water, the water competes with the weak acid or the weak base of the salt, as the case may be, with the liberation of alkali or acid. Evidently salts like sodium chloride whose acid and basic constituents are both strong will not suffer any hydrolysis.

A third and theoretically the simplest method of dealing with such hydrolysis is offered by the modern theory of acids and bases (vide Ch. XVIII, P. 294). It has been pointed out there that the ions are themselves acidic or basic and this lies at the root of salt solutions being acidic or basic. Hence, these types of hydrolysis, are often called cation hydrolysis and anion hydrolysis respectively.

We shall now discuss quantitatively the three types of hydrolysis:—(i) *The hydrolysis of a salt of a strong base and a weak acid; (ii) The hydrolysis of a salt of a weak base and a strong acid; and (iii) The hydrolysis of a salt of a weak base and a weak acid.*

(i) **Hydrolysis of a Salt of a Strong Base and a Weak Acid—** Salts such as potassium cyanide, sodium borate, sodium acetate, etc. fall in this class. The general equation for hydrolysis is—

$$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA$$
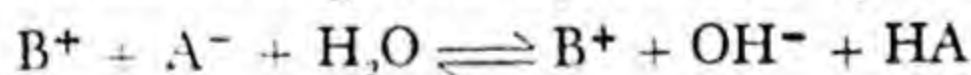
since the base BOH, being strong, may be regarded as completely ionised, and the acid HA, being weak and particularly in presence of the highly ionised salt BA, may be regarded as almost undissociated.

From the law of mass action, $\dfrac{[OH^-] \times [HA]}{[A^-] \times [H_2O]} = K$

Since the active mass of water, [H₂O] is constant,

$$K_h = \frac{[OH^-] \times [HA]}{[A^-]} = \frac{[free\ base] \times [free\ acid]}{[unhydrolysed\ salt]} \qquad \dots \qquad \dots \quad (7)$$

where K_h is called the hydrolysis constant.

There are also simultaneously other equilibria in the solution represented by—

$$[H^+] \times [OH^-] = K_w \dots (i) ; \quad \frac{[H^+] \times [A^-]}{[HA]} = K_a \dots (ii)$$

where K_w is the *ionic product* of water (P. 263) and K_a is the *dissociation constant* of the weak acid, HA (P. 259)

$$\frac{K_w}{K_a} = \frac{[OH_-] \times [HA]}{[A^-]} = \frac{[free\ base] \times [free\ acid]}{[unhydrolysed\ salt]} = K_h \quad \dots \quad (8)$$

i. e. the hydrolysis constant is the ratio of the ionic product of water to the dissociation constant of the weak acid.

Let 1 mol of the salt BA, be present in v *litres* $(c = 1/v)$ of the solution and let h be its *degree of hydrolysis* (*i.e.* fraction hydrolysed). Then, the number of mols of unionised salt is $1 - h$, and the number of mols of free acid and base is both equal to h.

$$\therefore \quad K_h = \frac{[OH^-] \times [HA]}{[A^-]} = \frac{\frac{h}{v} \times \frac{h}{v}}{\frac{1-h}{v}} = \frac{h^2}{(1-h)v} = \frac{h^2 c}{(1-h)} \quad \dots \quad (9)$$

$$\therefore \quad \frac{h^2}{(1-h)v} = K_h = \frac{K_w}{K_a} \quad \dots \quad \dots \quad (10)\text{-XVII}$$

EXAMPLE 5. *Calculate the degree of hydrolysis of a decinormal KCN solution at 25°C. The dissociation constant of HCN is 7.2×10^{-10} and the ionic product of water is 10^{-14}*

$$\frac{h^2 c}{(1-h)} = K_h = \frac{K_w}{K_a} \quad \text{or} \quad \frac{h^2 \times 1}{(1-h)} = \frac{10^{-14}}{7.2 \times 10^{-10}}$$

Neglecting h in the denominator, and solving we get $h^2 \times 1 = 1.39 \times 10^{-5}$ $\therefore$ $h = 1.18 \times 10^{-2} = 1.18$ *per cent.*

(ii) **Hydrolysis of a Salt of a Weak Base and a Strong Acid—** Examples of such salts are copper sulphate, ferric chloride, ammonium chloride, etc. A similar line of reasoning and equations as the foregoing applies here except that the base is here weak instead of the acid. Taking the general case of a salt BA, whose base BOH is weak, we have

$$B^+ + A^- + H_2O \rightleftharpoons BOH + H^+ + A^-$$
$$(1-h) \qquad \qquad h \quad\ \ h$$

$$\therefore \quad K_h = \frac{[H^+] \times [BOH]}{[B^+]} = \frac{[free\ acid \times free\ base]}{[unhydrolysed\ salt]} \quad \dots \quad (11)$$
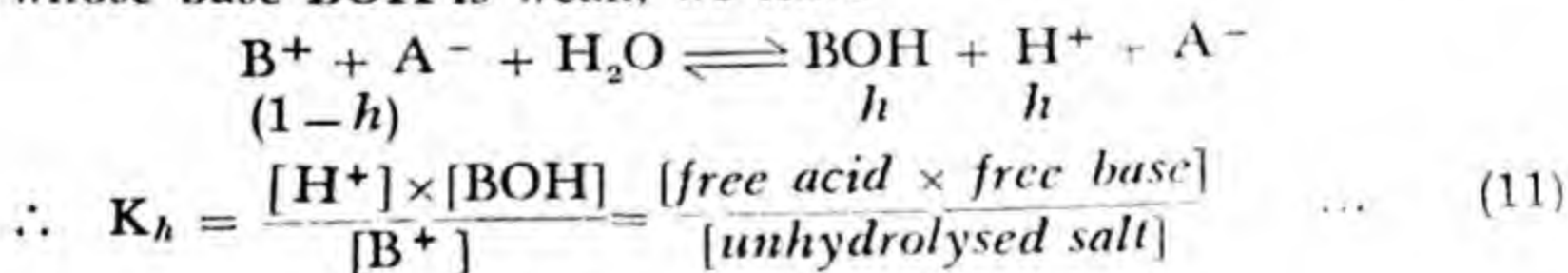
Also, there are existing the following equilibria—

$$[H^+] \times [OH^-] = K_w; \quad \frac{[B^+] \times [OH^-]}{[BOH]} = K_b \text{ (Dissociation Const.)}$$

$$\therefore \quad \frac{K_w}{K_b} = \frac{[H^+] \times [BOH]}{[B^+]} = K_h \text{ (Hydrolysis Const).}$$

If the degree of hydrolysis be h, the concentrations of B^+, H^+ and BOH are respectively $\frac{1-h}{v}$, $\frac{h}{v}$ and $\frac{h}{v}$ where v

litres are the volume containing 1 mol of the salt.

$$\therefore \quad K_h = \frac{[H^+] \times [BOH]}{[B^+]} = \frac{h^2}{(1-h)v} = \frac{h^2c}{(1-h)} \left[\text{Since } c = \frac{1}{v} \right]$$

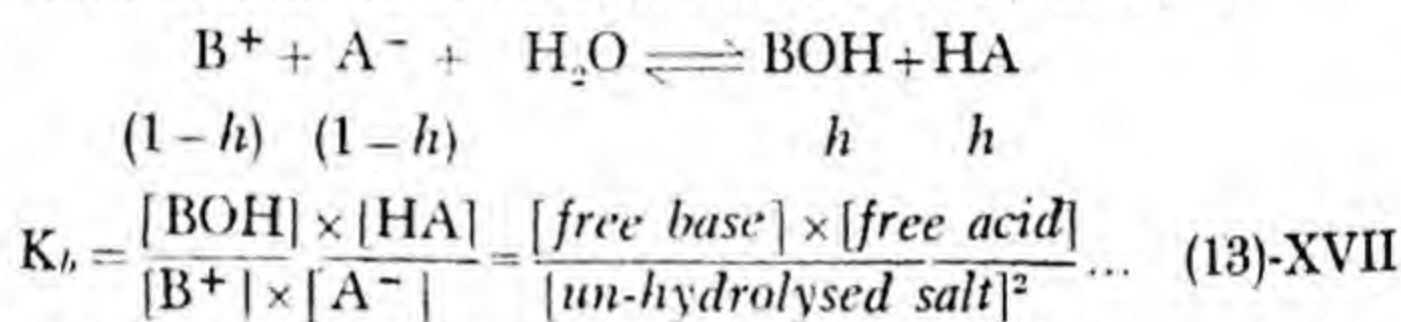$$\therefore \quad \frac{h^2}{(1-h)v} = K_h = \frac{K_w}{K_a} \qquad \ldots \qquad \ldots \quad (12)\text{-XVII}$$

EXAMPLE 6. *Calculate the degree of hydrolysis of a centinormal ammonium chloride solution. Given the dissociation constant for ammonia is 4×10^{-5} and ionic product of water is 1×10^{-14},*

$$\frac{h^2c}{1-h} = K_h = \frac{K_w}{K_a} \text{ or, } \frac{h^2 \times \cdot 01}{1-h} = \frac{1 \times 10^{-14}}{4 \times 10^{-5}}$$

or $h = 1 \cdot 58 \times 10^{-4}$ i.e. 0·0158 per cent.

(iii) Hydrolysis of a Salt of a Weak Acid and a Weak Base— Examples of such salts are aniline acetate, ammonium acetate, ferric formate, etc. Taking the general case of a salt BA, where both the acid and the basic constituents are weak, we have

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

$$(1-h) \quad (1-h) \qquad \qquad h \qquad h$$

$$K_h = \frac{[BOH] \times [HA]}{[B^+] \times [A^-]} = \frac{[free\ base] \times [free\ acid]}{[un\text{-}hydrolysed\ salt]^2} \quad \ldots \quad (13)\text{-XVII}$$

Also, there are co-existing the following equilibria—

$$\frac{[H^+] \times [A^-]}{[HA]} = K_a; \quad \frac{[OH^-] \times [B^+]}{[BOH]} = K_b; \quad [H^+] \times [OH^-] = K_w$$

$$\frac{K_w}{K_a \cdot K_b} = \frac{[HA] \times [BOH]}{[B^+] \times [A^-]} = \frac{h^2}{(1-h)^2} = K_h$$

$$\text{or, } \frac{h}{(1-h)} = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} \qquad \ldots \qquad \ldots \quad (14)\text{-XVII}$$

Hence, the degree of hydrolysis, in this case, is independent of concentration of the salt. It may however be pointed out that the solution is not neutral but is acidic or alkaline according as K_a is greater or less than K_b, and is neutral (i.e. $[H^+] = [OH^-]$) when K_b and K_a are equal.

EXAMPLE 7. *Calculate the degree of hydrolysis of ammonium acetate, dissociation constant for NH_4OH is 4×10^{-5}, and that for CH_3COOH 1.8×10^{-5}.*

$$\frac{h}{1-h} = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{4 \times 1 \cdot 8 \times 10^{-10}}} \quad \therefore \quad h = 0 \cdot 37 \text{ per cent.}$$

Experimental Determination of Hydrolysis —Any method for the determination of free acid or free base in a solution may well serve for the determination of the degree of hydrolysis. Thus, by comparing the catalytic effect of a salt solution on the rate of inversion of cane sugar or on the rate of saponification of methyl acetate, with the effect in presence of a standard acid or

base, the hydrogen ion concentrations of the salt solutions become known and therefrom, the degree of hydrolysis and hydrolysis constants are calculated. Other methods involving conductivity measurements or hydrogen ion concentration measurements can also be used.

EXAMPLE 8. *Assuming that the dissociation constants of ammonia and acetic acid are both equal to 1×10^{-5}, calculate the concentration of H ion in the following solution :—(a) A mixture containing 5 c.c. $N/10$ acetic acid and 5 c.c. $N/10$ caustic soda. (b) A mixture containing 5 c.c. $N/10$ ammonia and 5 c.c. $N/10$ hydrochloric acid. (Ionic product for water $=1 \times 10^{-14}$).*

(a) The resulting solution is a $N/20$ ($0.05N$) sodium acetate solution hydrolysing according to the equation :—$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

Applying the equation,

$$\frac{h^2 c}{1-h} = Kh = \frac{K_w}{K_a},$$

we have, $\frac{h^2 \times .05}{1-h} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$

Neglecting h in denominator, $h^2 = 2 \times 10^{-8}$, or $h = 1.41 \times 10^{-4}$

∴ $[OH^-] = hc = 1.41 \times .05 \times 10^{-4} = 7.05 \times 10^{-6}$

∴ $[H+] = K_w/[OH^-] = 10^{-14}/7.05 \times 10^{-6} = 1.42 \times 10^{-9}$

(b) The resulting solution is a $N/20$ ($= .05N$) solution of ammonium chloride.

∴ $\frac{h^2 \times .05}{1-h} = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-5}}$, ∴ $h = 1.41 \times 10^{-4}$

∴ $[H+] = h/v = h \times c = 1.41 \times .05 \times 10^{-4} = 0.70 \times 10^{-5}$

SOLUBILITY PRODUCT

Introduction —The solubility of any substance is little affected by the presence of another solute, a notable exception being electrolytes with a common ion. For example, one litre of water dissolves 12 gms of lead chloride at 30°C, whereas one litre of normal potassium chloride solution dissolves only about 0.5 gms of lead chloride. This is quite striking if we recall that the solubility of any other solute without a common ion, say, lead sulphate would not change by 5 or 10 per cent by the same change of solvent. This has received a quantitative explanation from the principle of solubility product which we discuss below.

Fig. 95—Equilibrium between Ions and Precipitate

Solubility Product Principle—Although the law of mass action does not apply to the process of electrolytic dissociation except in the case of weak electrolytes (*vide* P. 261), it applies with considerable accuracy on saturated
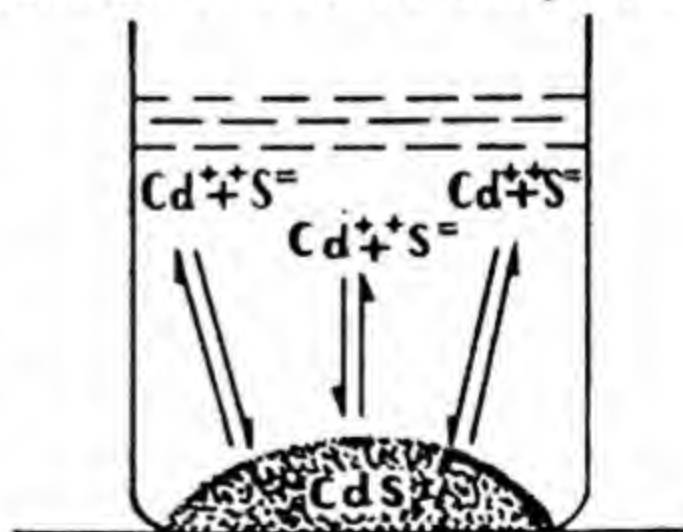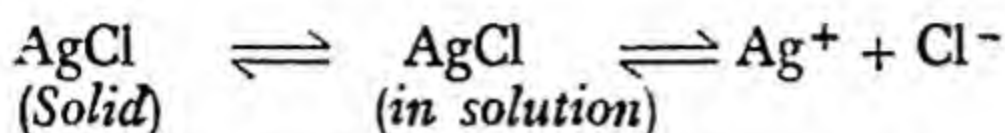
solutions of sparingly soluble salts. The dissociation in the typical case of a saturated solution of silver chloride may be represented as—

$$AgCl \rightleftharpoons AgCl \rightleftharpoons Ag^+ + Cl^-$$
(*Solid*)   (*in solution*)

Applying the law of mass action, we get

$$\frac{[Ag^+] \times [Cl^-]}{[AgCl]} = K \text{ or, } [Ag^+] \times [Cl^-] = K \times [AgCl]$$

The concentration of unionised solute, [AgCl] is *constant* since it is in equilibrium with *solid silver chloride*, whose active mass is indeed constant.

$$\therefore \quad [Ag^+] \times [Cl^-] = K_s = \text{const.} \quad \dots \quad \dots \quad (15)\text{-XVII}$$

This constant K_s is called the *solubility product of* AgCl.

Taking the general case of a sparingly soluble salt BA, whose solubility is s moles per litre, the concentrations of $[B^+]$ and $[A^-]$—*assuming complete dissociation*—are necessarily each equal to s *gm ion per litre*.

$$\therefore \quad \text{Solubility Product, } K_s = [B^+][A^-] = s^2, \quad (16)\text{-XVII}$$

i.e. the solubility product of a sparingly soluble binary electrolyte is simply the square of its solubility in pure water expressed in gram mols per litre. Thus, at 20°C AgCl dissolves to the extent of 1.3×10^{-5} mols per litre; therefore, its solubility product, K_s is $(1.3 \times 10^{-5})^2$ *i.e.* 1.7×10^{-10}.

Salts giving more than Two Ions—If the salt is of the type $A_x B_y$, $(A_x B_y \rightleftharpoons xA^+ + yB^-)$, the solubility product,

$$K_s = [A^+]^x \times [B^-]^y \quad \dots \quad \dots \quad \dots \quad \dots \quad (17)\text{-XVII}$$

Therefore, the *solubility product of a salt may be defined as the greatest possible product of the concentrations of its constituent ions in its saturated solution, each concentration term being raised to a power representing the number of ions of that type formed by the dissociation of one molecule of the salt.* Evidently, the solubility product of a salt is constant only at a particular temperature.

It is customary to express the concentrations of the ions in the calculation of solubility product in *gram ion per litre, i.e.* formula weight per litre, and not in gm equivalent per litre (*see examples below*). This is a very unusual convention in physical chemistry and should be carefully noted for computational purpose.

EXAMPLE 9. *The solubility of chalk is 0·0305 gms per 1000 c.c. of solution. Calculate its solubility product.*

     Mol. wt. of $CaCO_3 = 100$

$$\therefore \quad \text{Solubility, } s = 0.0305 \text{ gms per litre} = 3.05 \times 10^{-4} \text{ mols/litre.}$$

$$\text{Solubility product } K_s = s^2 = 9.3 \times 10^{-8}$$

EXAMPLE 10. *The solubility of CaF_2 is 0.0002 mol per litre. Find the solubility product.*

Since one molecule CaF_2 furnishes 1 Ca and 2F-ions

$[Ca^{++}] = 0.0002$ gm ion/litre : $[F^-] = 0.0004$ gm ion/litre

$\therefore$ Sol. product $= [Ca^{++}] [F^-]^2 = 0.0002 \times (0.0004)^2 = 3.2 \times 10^{-12}$

Solubility and Solubility Product —The concept of solubility (*vide* P. 168) as the amount of a solute dissolved per 100 gms of a solvent, can not serve the same purpose as the solubility product. The term solubility is applicable to all solutes, whereas solubility product has a meaning only with reference to an electrolyte. The most important difference is—as should be shortly pointed out—that the solubility of an electrolyte is diminished by the presence of a common ion, but the solubility product nevertheless remains constant. The relation between these two terms is presently discussed.

The Effect of a Common Ion —The effect on the solubility of a salt of the presence of another salt with a common ion can be easily calculated. Thus, if we add KCl to a solution of AgCl, we should have according to the solubility product principle,

$$[Ag^+] \times [Cl^-] = K_s = s^2 \qquad \cdots$$

But the chloride ion is supplied by both KCl and AgCl and so, if the concentration of KCl be c and the new solubility of AgCl be s', we should have, since the salts are completely dissociated, s' and $s' + c$ as the final concentrations of Ag^+ and Cl^- ions respectively in the saturated solution. But the product of the concentrations of these two ions, no matter what the source of these ions may be, must be equal to the solubility product and so we should have

$$(s') \times (s' + c) = K_s = s^2 \qquad \cdots \qquad \cdots \quad (18)\text{-XVII}$$

where the concentrations are expressed in gram mols or gram ions per litre. Similar equations for the more complicated cases of unsymmetrical types of salts can be easily deduced.

EXAMPLE 11. *Solubility of lead sulphate in water is 1.03×10^{-4}; calculate its solubility in a centinormal solution of sulphuric acid.*

Solubility product $K_s = s^2 = (1.03 \times 10^{-4})^2 = 1.06 \times 10^{-8}$

$c = 0.01 N = 0.005$ molar; substituting proper values in the equation, $s' \times (s' + c) = s^2$, we have $s' \times (s' + 0.005) = 1.06 \times 10^{-8}$.

Neglecting s' in the second term being small in comparison to 0.005, we have $s' = 2.1 \times 10^{-6}$.

It follows from equation (18) that the solubility for a symmetrical salt of the type BA would be equally diminished by adding the same concentrations of A^+ or B^- ions. This deduction of the theory of solubility product has been tested by Noyes for sparingly soluble thallous chloride, in presence of excess of thallous nitrate and also of hydrochloric acid. His results are given in the table, which show good agreement with theory.

Solvent	Solubility of TlCl in mol. per litre
Water	0·0161
0·0283 (N) HCl	0·0083
0·0283 Tl (NO$_3$)	0·0084
0·147 (N) HCl	0·0032
0·147 Tl (NO$_3$)	0·0032

The theory of solubility product is most useful in the case of *sparingly soluble salts* since their saturated solutions are dilute ones and so, (*i*) the law of mass action is obeyed more accurately, and (*ii*) the salts may be regarded as practically completely ionised so that the concentration of the unionised solute is negligible in comparison with the ions. Some data on solubility product are collected in tables to follow.

SOLUBILITY PRODUCT AND ANALYTICAL CHEMISTRY

Precipitation and Solubility product—Since precipitation is governed by the principle of solubility product, the latter receives important applications in the field of analytical chemistry. For example, if to a solution of cuprous salt, increasing amounts of chloride ion are gradually introduced, precipitation would start as soon as the product of $[Cu^+] \times [Cl^-]$ exceeds the solubility product of cuprous chloride. On adding more chloride ion, precipitation would continue such that the $[Cu^+] \times [Cl^-]$ in solution remains equal to the solubility product of cuprous chloride. So, as the chloride ion concentration increases, the residual cuprous ion concentration decreases, and by adding excess of the precipitating ion (here Cl^- ion), the residual copper in solution can be reduced to a negligibly small value. This is the reason why excess of precipitants has to be used in quantitative analysis. This picture of precipitation is extremely helpful to get an understanding of the different procedures of analytical chemistry.

Analytical Group I : The Insoluble Chlorides —Silver, lead, and mercurous mercury belong to this group as their chlorides are sufficiently insoluble whereas chlorides of all other common metals are soluble. The solubility product (20°C) values are shown below:

Salt	Solubility, s mols/litre	Solubility Product, K_s
AgCl	$1·3 \times 10^{-5}$	$[Ag^+][Cl^-] = 1·8 \times 10^{-10}$
Hg$_2$Cl	9×10^{-7}	$[Hg_2^{++}][Cl^-]^2 = 1·1 \times 10^{-18}$
PbCl$_2$	$3·9 \times 10^{-2}$	$[Pb^{++}][Cl]^2 = 1·7 \times 10^{-4}$

This gives a quantitative picture of the precipitation of these three salts as chlorides. It should be noted that K_s for lead chloride is very much higher than those of the other two and this explains why the precipitation of lead chloride is not as complete as those of HgCl and AgCl.

Things however are often much more complicated than that suggested by the above table due to the coexistence of other ionic equilibria. For example, in the above table the solubility product of $PbCl_2$ is lower than that calculated from the corresponding solubility value (i.e. $K_s < s^2$). This is due to the fact that a good portion of the lead ions in solution does not exist as lead ions but exists as $Pb(OH)^+$ ions owing to hydrolysis and so the latter do not contribute to the solubility product of $PbCl_2$. Complications of this type exist in many cases and so, as we shall see also in the next table, the solubility in many instances is much more than the theoretically expected value, viz. square root of solubility product (eqn. (16)-XVII). Further, though the residual silver ions would be expected to be very small owing to the low value of K_s of AgCl, too much chloride ion should not be added, as AgCl then tends to dissolve by the equilibrium $AgCl + Cl^- \rightleftharpoons AgCl_2^-$.

The dissolution of AgCl in ammonia is due to the formation of a complex as shown below.

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$$
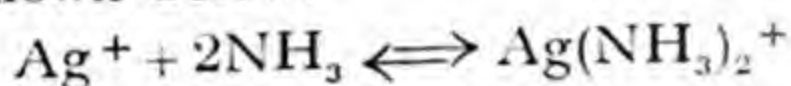
The equilibrium constant for the above reaction (its reciprocal being also called instability constant of the complex) is 1.7×10^7, showing that it is practically fully displaced towards the right. This explains the powerful dissolving action of ammonia on AgCl.

Application of H_2S in Group Separation—Sulphuretted hydrogen dissolves in water and ionises as a weak acid, $H_2S \rightleftharpoons 2H^+ + S^{--}$, with $K_a = 1.1 \times 10^{-22}$. Now, the solubility of $[H_2S]$ under usual laboratory conditions is about 0.1 molar and so the $[S^{--}]$ ion concentration is given by (ii).

(i) $\dfrac{[H^+]^2 \times [S^{--}]}{[H_2S]} = 1.1 \times 10^{-22}$; (ii) $[S^{--}] = \dfrac{1.1 \times 10^{-23}}{[H^+]^2}$

It is thus seen that the sulphide ion concentration depends on the acidity of the solution and can be varied over an enormous range from 10^{-23} to over one mol per litre if the acidity of the solution changes from about normal acid to highly alkaline conditions.

Precipitation of Gr. II Metals—Evidently, the more acid a solution, the lower would be $[S^{--}]$. Ordinarily, Group II is precipitated by bubbling H_2S through a solution which is 0.4N in hydrochloric acid. In such a solution the concentration of sulphide ion according to equation (ii) is 6×10^{-23}M and so only the extremely insoluble sulphides would precipitate under such conditions. The matter is however highly complicated due to hydrolysis and other side effects and only qualitative agreement with the simple theory of solubility product is obtained. The solubility (s) and solubility product (K_s) values at 25° are given in the following table. The solubility products of the sulphides of Zn, Mn, etc. being comparatively high, they are not exceeded by such small concen-

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tration of S^{--} ions as are supplied by this very small dissociation of H_2S and so they are not precipitated at all.

Sulphide	Colour	Solubility, s mols/litre	Solubility Product $[M^{++}] \times [S^{--}]$
CdS	yellow	3.1×10^{-14}	7.1×10^{-28}
PbS	black	2.2×10^{-14}	3.4×10^{-28}
CuS	black	2.2×10^{-17}	3.5×10^{-42}
HgS	black	2.1×10^{-23}	3×10^{-54}
FeS	black	1.3×10^{-6}	3.7×10^{-19}
ZnS	white	3.1×10^{-9}	6.9×10^{-26}
NiS	black	4×10^{-10}	1.1×10^{-27}

If the bubbling of H_2S is slowly done, the sulphides will precipitate roughly in the reverse order of their solubilities, that is, in the order mercuric sulphide (black), copper sulphide(black), arsenic sulphides (yellow), antimony sulphides (orange), tin sulphides (yellow or brown), bismuth sulphide (deep brown), lead sulphide (black) and cadmium sulphide (yellow) because their solubility products will be exceeded in this order. It should be noted however that precipitation leads to increase in acidity, for example, by the reaction, $Cd^{++} + H_2S \rightleftharpoons CdS + 2H^+$, which will interfere with the effectiveness of precipitation, particularly of the tail-enders such as PbS and CdS, and so it is necessary when precipitation appears to be complete to dilute the solution to reduce the acidity to the optimum value and again bubble more H_2S to complete the precipitation of PbS and CdS.

Precipitation of Group III—After separating the precipitated sulphides by filtration the dissolved H_2S is boiled off as it would form S^{--} ions later by reacting with ammonia. The filtrate is now made alkaline with ammonia (0·1N) and ammonium chloride (3N) (see next section). The concentration of OH^- ions is extremely low and is about $6 \times 10^{-7}N$ as can be easily calculated from the K_b of ammonia ($K_b = 1.8 \times 10^{-5}$). Such low OH^- is just enough to precipitate the hydroxides of Fe, Al and Cr and none else.

After separating the hydroxides. H_2S is passed through the ammoniacal solution. Ammonium sulphide is formed which being a salt ionises to produce a large concentration of S^{--} ions. large enough for the precipitation of the sulphide of zinc. cobalt. nickel and manganese.

EXAMPLE 12. *Will decinormal Mn containing N/100 acid be precipitated by passing H_2S?*

Putting $[H+]=0.01$ in equation (*ii*). we get $[S^{--}]=10^{-19}$. Thus, the maximum value of $[Mn^{++}] \times [S^{--}]$ in the given solution is $0.1 \times 10^{-19} = 10^{-20}$ which is about one hundred thousand times lower than the sol. product of MnS, 1.4×10^{-15}. So, no precipitation will occur.

NH_4Cl as an Adjunct to NH_4OH —NH_4OH will normally precipitate Mg^{++} as hydroxide. but in the presence of NH_4Cl, Mg^{++} Zn^{++}. Mn^{++}, etc. are not precipitated which is explained as

follows.   Ammonium chloride depresses the dissociation of ammonium hydroxide ($NH_4OH \rightleftharpoons NH_4^+ + OH^-$) by the introduction the common ion NH_4^+, producing a 'buffer solution' of lower OH^- ion concentration.   This low concentration of hydroxyl ion can still exceed the solubility product of the hydroxides of Fe, Al, etc., but not those of Zn, Mn or Mg, and so, the latter hydroxides whose solubility products are high are not precipitated by this reagent in Gr. III (a).

EXAMPLE 13.   *Calculate the concentration of OH^- ion in a 0·1 N ammonia solution containing 3 N NH_4Cl, given $1·8 \times 10^{-5}$ to be the dissociation constant of ammonia.*

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = 1·8 \times 10^{-5}$$

Since the ammonia is very little dissociated, we should have $[NH_4OH]$ $=0·1$ and $[NH_4^+] = 3$, which substituted in the above equation gives $[OH^-]$ $=1·8 \times 10^{-5} \times 1/3 = 6 \times 10^{-7}$.

Preparation of Pure NaCl—The precipitation of sodium chloride by the introduction of HCl in a saturated solution of common salt, is also due to a similar cause.   The HCl introduces a high concentration of Cl^- ions and so, in the solution the existing ionic product $[Na^+] \times [Cl^-]$ exceeds the solubility product of sodium chloride, which therefore falls out in the pure state.

EXAMPLE 14.   *The solubility product of lead sulphide is $3·4 \times 10^{-28}$. What sulphide ion concentration will be required to just precipitate lead sulphide from an one-thousandth molar solution of a lead salt assuming complete dissociation.*

In the given solution, the concentration of lead ion $[Pb^{++}]$ is 0·001 M.   We have to find out the concentration of sulphide ion, $[S^{--}]$ which just reaches the solubility product of lead sulphide, PbS.

i.e. $[Pb^{++}] \times [S^{--}] = 3·4 \times 10^{-28}$ or $[·001] \times [S^{--}] = 3·4 \times 10^{-28}$

or $[S^{--}] = 3·4 \times 10^{-25}$

EXAMPLE 15.   *Calculate how much hydrochloric acid is to be added to a 0·001 molar lead salt solution to just prevent precipitation when saturated with H_2S. Assume complete dissociation for hydrochloric acid and the lead salt, given sol. product for H_2S is $1·1 \times 10^{-23}$ and for PbS is $3·4 \times 10^{-28}$.*

$[S^{--}]$ necessary to just start precipitation of PbS is $3·4 \times 10^{-25}$ (See previous example). The acid should supply such hydrogen ion conc. as produces the above value of $[S^{--}]$. Now for $H_2S \rightleftharpoons 2H^+ + S^{--}$, we have

$[H^+]^2 \times 3·4 \times 10^{-25} = 1·1 \times 10^{-23}$

or $[H^+] = 5·7$ mol/litres i.e. any acid strength stronger than 5·7 normal will completely prevent precipitation of lead from the above solution.

EXAMPLE 16.   *The solubility of $BaSO_4$ is $2·3 \times 10^{-4}$ gms. per 100 c.c. of water. Calculate the percentage error in washing 0·2 gm. of $BaSO_4$ precipitate with (a) 1 litre of water and (b) 1 litre of N/100 H_2SO_4 [Ba=137, S=32, O=16]*

(a) $BaSO_4$ dissolved per litre $=2·3 \times 10^{-4} \times 10 = 2·3 \times 10^{-3}$ gms.

Percentage error $= \dfrac{2·3 \times 10^{-3}}{0·2} \times 100 = 1·15\%$

(b) Solubility of $BaSO_4$ (s) $=2·3 \times 10^{-3}/233·4$ mols/litre. [Since Mol. wt. $=233·4] = ·985 \times 10^{-5}$ mols/litre.

Solubility product, $K_s = s^2 = 0·971 \times 10^{-10}$

Let x gm. $BaSO_4$ dissolve in 1 litre of $N/100$ H_2SO_4

$\therefore$ $[Ba++] = x/233.4$ mols/litre.

Now, the sulphate ions are supplied from two sources; by the dissociation of sulphuric acid in solution and by the dissociation of the salt $BaSO_4$. The former source gives $[SO_4^{--}]$ ions of $.01$ $(N) = \frac{1}{2} \times .01$ molar and the latter $x/233.4$ molar concentration.

$\therefore$ Total conc. of $[SO_4^{--}]$ ions $= [(x/233.4) + 0.01/2]$ gm. ion/litre.

Inserting values in the equation, $K_s = [Ba++] \times [SO_4^{--}]$

$0.971 \times 10^{-10} = (x/233.4) \times [(x/233.4) + .005]$

Or, $x = 4.53 \times 10^{-6}$ gms.

$\therefore$ percentage error $= (x/0.2) \times 100 = .00227\%$.

EXAMPLE 17. *The dissociation constant of acetic acid is* 1.8×10^{-5}, *calculate the* H^+ *ion conc. of a* 0.01 (N) *acid solution, and its pH.*

$$\frac{a^2 c}{1-a} = K \quad \text{or,} \quad \frac{a^2 \times .01}{(1-a)} = 1.8 \times 10^{-5}; \text{ neglecting } a \text{ in the denomi-}$$

nator, and solving we get, $a = 4.24 \times 10^{-2}$

$[H^+] = a/v = ac = 0.01 \times 4.24 \times 10^{-2} = 0.000424$ gm. ion/litre.

$pH = -\log 0.000424 = -\log 4.24 \times 10^{-4} = 3.37$.

Exercise

1. Deduce Ostwald's dilution law and discuss its limitations.

2. How do you experimentally determine the dissociation constant of acetic acid?

3. The solubility of lead iodide is 0.7 gm. per litre and that of lead chloride is 1.1×10^{-3} mol. per litre. Calculate their solubility products. $[1.4 \times 10^{-8}; 5.3 \times 10^{-9}]$

4. What do you understand by the term "solubility product"? How does it explain the different reactions in analytical chemistry.

A litre of a saturated solution of silver bromate contains 0.0081 gm. mol. of the salt : $c = 0.0785$ mol of silver nitrate is then added. Calculate the new solubility "S" of silver bromate assuming both salts to be completely dissociated in solution. $[0.00081$ mol/litre.$]$

5. The solubility of barium sulphate at $28°C$ is 0.002334 gram per litre. Calculate the solubility product of the salt, assuming it to be completely ionised. $[1 \times 10^{-10}]$

What will be the solubility of barium sulphate at $28°C$ in an ammonium sulphate solution containing 13.2 grams of ammonium sulphate per litre, assuming complete dissociation? $[Ba = 137.1]$
$[233 \times 10^{-9}$ gm/litre approx.$]$

6. The dissociation constant of NH_4OH is 1.8×10^{-5}. The solubility product of magnesium hydroxide is 1.22×10^{-11}. How many gms. of solid NH_4Cl must be added to a mixture of 50 c.c., (N) NH_4OH solution and 50 c.c. (N) $MgCl_2$ solution so that precipitate of $Mg(OH)_2$ just disappears. It is assumed that the volume of the solution is not changed by dissolving the solid NH_4Cl and that dissociation of the neutral salt is complete.
$[1.82$ $(N)NH_4Cl; 9.74$ gms per 100 c.c.$]$

7. On the basis of the electrolytic dissociation theory, explain clearly the use of dilute hydrochloric acid in the second group and of ammonium chloride in the third group of systematic qualitative analysis of inorganic bases.

8. Explain the law of mass action and apply it to the electrolytic dissociation of acetic acid. How will you determine the degree of dissociation of acetic acid?

9. Explain what do you understand by the term solubility product. Knowing that the solubility of AgCl is 0·0015 gm. per litre at 18°C, calculate (a) the solubility product of this salt admitting that it is totally ionised at the concentration indicated, that is to say, in very dilute solution; (b) the quantity of AgCl which remains dissolved if one adds a solution of NaCl such that the total concentration of it is 0·4585 gm of NaCl per litre, [Na−23·4; Cl−35·5; Ag−108·0]

$$[1·09 \times 10^{-10}; \quad 2·01 \times 10^{-9} \text{ gm/litre}]$$

10. Comment on the fact that magnesium hydroxide is soluble in a solution of ammonium chloride but not either in sodium or potassium chloride solutions.

11. Why is a solution of sodium carbonate alkaline and a solution of copper sulphate acidic to litmus?

12. The degree of hydrolysis of 0·01N solution of KCN is 4 per cent. What is the value of the hydrolytic constant? How is this constant related to the dissociation constant of hydrocyanic acid. $[1·667 \times 10^{-5}]$

13. On what experimental evidence is it concluded that water is electrolytically dissociated to a small extent? What is conductivity water? How is it prepared in the laboratory?

14. Suppose by some mechanism all the hydrogen ions and hydroxyl ions present in a sample of pure water is instantaneously removed. Will this treated sample of water be a perfect non-conductor? Discuss thoroughly.

15. Calculate how many hydrogen ions are present in one-millionth part of one c.c. of pure water at 25°C. [60·3 million]

16. The ionic product of water increases with temperature. How does this fact affect the amount of hydrolysis of a salt and also the pH value of a dilute solution of (i) a strong acid and (ii) a strong base.

17. (a) Prove that the ratio of the H+ ion concentrations of two very weak acids at the same dilution is independent of concentration.

(b) If the ratio of their dissociation constants be 100, prove that the difference in pH value of any pair of solutions of the two acids at equivalent dilution is one unit of pH.

18. The dissociation constants of ammonia and acetic acid being equal, what would be the pH of an ammonia solution, if that of an acetic acid solution of equal strength is 3·2, given K_w for water is 10^{-14}. What is the unit of K_w? [10·8; conc.⁻²]

CHAPTER XVII

ELECTROMOTIVE FORCE

Galvanic Cells—Cells which are capable of producing electric current at the expense of some physicochemical process going on inside it are called galvanic cells. The potential difference which exists between the two electrodes of a cell *on open circuit* is called the E. M. F. of the cell.

The origin of an E. M. F. in a cell is not difficult to understand. Examining a very familiar type of cell, say, the Daniell cell, we find that it essentially consists of two electrodes, one of zinc and the other of copper dipped into zinc sulphate and copper sulphate solutions respectively, the two solutions being separated by a porous partition. The zinc sulphate solution contains zinc ions, Zn^{++} and so, when metallic zinc is placed in contact with it, a definite equilibrium between the solid zinc and Zn^{++} ions are produced owing to the establishment of the following equilibrium,

$$Zn^{++} + 2\epsilon \rightleftharpoons Zn$$
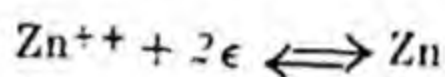
where ϵ represents an electron. Of course, the electrons are present in the solid, and are responsible for its conductivity. So, whenever zinc is in contact with zinc sulphate solution, a definite pressure of electron is created at the interface. Similarly, a definite electron pressure is created at the interface between copper and copper sulphate solution, owing to the establishment of the equilibrium,

$$Cu^{++} + 2\epsilon \rightleftharpoons Cu$$
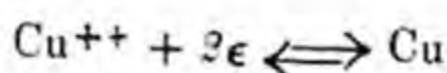
It so happens in this case that the electron pressure on the zinc electrode is higher than that of the copper electrode and so on connecting these externally with a piece of wire a steady stream of electrons flows through this conductor from zinc to copper. In order to maintain this flow of electrons more zinc ionises and more copper is deposited with the net effect that a chemical reaction has taken place by the passage of the current, which is represented by the equation,

$$Cu^{++} + Zn = Cu + Zn^{++}$$

Therefore, we can regard all electric cells as devices where the energy of a physicochemical process is converted into electrical energy.

Reversible and Irreversible Cells—In order to be able to apply exact thermodynamic methods to cell reactions it has been found necessary to distinguish between reversible and irreversible cells, because the thermodynamical treatment is only applicable to the former type of cells. We have shown in the section of thermodynamics (P. 127) that the definition of reversibility necessitated two conditions: (*a*) that the process operates under a condition that the driving force is infinitesimally greater than the opposing force,

and (b) that the process can be completely reversed if an external force is applied which is infinitesimally greater than the driving force of the system. Any cell which satisfies these two conditions is a reversible cell.

Suppose to a Daniell cell we apply an external E.M.F. infinitesimally smaller than its own E. M. F. The cell reaction, $Cu^{++} + Zn \longrightarrow Cu + Zn^{++}$ will go on extremely slowly in the direction shown by the equation. After the reaction has gone forward to some extent, suppose we increase the external E.M.F. to be infinitesimally greater than the E.M.F. of the cell. The cell reaction will now go on in the reverse direction. $Cu + Zn^{++} \longrightarrow Cu^{++} + Zn$ and by maintaining the external applied E. M. F. long enough it is possible to restore the original condition. Such a cell is called a *reversible* cell. This cell, however, is not strictly reversible because we can never restore reversibly any diffusion which might have taken place through the porous partition during the functioning of the cell. However this cell is a fairly close approach to a reversible cell and for all theoretical purposes can be so treated.

From the above discussion it is apparent that if anything happens in any part of the cell which is not reversible, the cell itself becomes irreversible. In many cells gases are evolved. Evidently, we cannot restore back the gases with an applied external E. M. F. Such cells should be regarded as *irreversible*. Many other types of irreversible process are conceivable and any cell which operates even partly on any such process becomes irreversible.

Free Energy of Reversible Cells—It was shown in our study of thermorynamics (P. 137) that any chemical reaction reversibly conducted can yield some external work, and the *net work* performed in the process, if conducted reversibly, at constant temperature under a given pressure is equal to the decrease in free energy of the system, $-\triangle F$. In the science of electricity whenever a quantity of electricity is transported across a potential difference, electrical work equal to the product, quantity of electricity × potential difference is done. Since one faraday of electricity (**F**) is associated with one chemical equivalent, n**F** quantity of electricity needs be passed if the cell reaction concerns n chemical equivalents. If the E. M. F. of the cell is E, the electrical work is nFE. Therefore, we have,

Decrease in free energy=Electrical work done   ... (1)-XVIII

or, $-\triangle F = n\mathbf{F}E$;   or $\triangle F = -n\mathbf{F}E$ ... (2)-XVIII

This equation is of great importance as it gives an expression for free energy in terms of measurable quantities. To distinguish Faraday from free energy both of which are designated by capital F, we have used thicker type for the former.

Application of Gibbs-Helmholtz equation—The question now arises how much of the heat of reaction is converted into electrical enegry. Taking a concrete case of the Daniell cell, where the reaction is

$$Zn + Cu^{++} = Cu + Zn^{++}$$
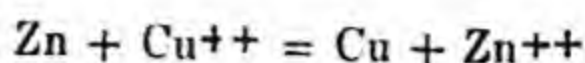
we might take a mol of copper sulphate in solution in a beaker and put a gram atom of zinc and measure the amount of heat which is evolved in the above reaction. We might also measure the E. M. F. of the Daniell cell where the same reaction is carried out reversibly and multiply it by $2F$ (since 2 chemical equivalents are involved in the above reaction) and convert it into calories. Will these two heat terms be equal? Thermodynamics supply a straightforward answer to this question. According to a form of Gibbs-Helmholtz equation [(eqn. (19)-X].

$$\triangle F = \triangle H - T \triangle S$$

$$\triangle F - \triangle H = - T \triangle S$$

Since we measure $\triangle H$ in a calorimeter and $\triangle F$ by E. M. F. measurement, these two terms $\triangle F$ and $\triangle H$ will generally not be equal but their difference is equal to $- T \triangle S$, where $\triangle S$ is the increase in entropy in the above chemical reaction.

According to Gibbs-Helmholtz equation, we have [(18)-X]

$$\triangle F = \triangle H + T \left(\frac{\partial \triangle F}{\partial T} \right)_P$$

Substituting $\triangle F = - n F E$, and with proper transposition, we get,

$$- \triangle H = n F E - n F T \left(\frac{\partial E}{\partial T} \right)_P \qquad \dots \quad (3)\text{-XVIII}$$

where $\left(\frac{\partial E}{\partial T} \right)_P$ is the rate of change of E. M. F. with temperature, i.e. temp. co-efficient of E. M. F. This equation correlates the heat of reaction at constant pressure. $- \triangle H$ with the E. M. F. and the temperature co-efficient of the E. M. F. of the cell. It would be observed from the above equation that if the E. M. F. of a cell increases with temperature, the electrical energy produced ($n F E$) is greater than the chemical energy ($- \triangle H$) of the reaction: on the other hand, with negative temperature co-efficient of E.M.F. the reverse is true. In case the cell does not change its voltage with temperature, the heat of reaction at constant pressure, $- \triangle H$ will be equal to the decrease in free energy, $- \triangle F$ i.e., $n F E$, and during working the cell will neither absorb nor evolve any heat, as the electrical energy produced is exactly equal to the chemical energy of the reaction.

We can test the above equation by calculating $- \triangle H$ from

E. M. F. data and comparing it with the value measured calorimetrically, as is done below for the reaction,

$$Zn + 2AgCl = ZnCl_2 \text{ (0·555 molal)} + 2Ag.$$
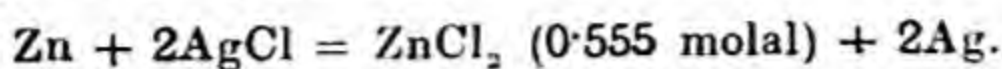
The electric cell corresponding to the above chemical reaction is easily constructed by dipping a zinc electrode and a Ag, AgCl electrode (silver coated with silver chloride) in a 0·555 molal zinc chloride solution. The observed E. M. F. of the cell at 0°C is 1·015 volts and its temperature co-efficient of E. M. F. is $= 4·02 \times 10^{-4}$ volts per degree. These values are substituted in the above equation, and converting the electrical work term which is in Joules into calories by dividing with 4·1833, we obtain $-\triangle H = 51,990$ calories. The calorimetrically measured heat of reaction for the same is 52,050 calories, which is in excellent agreement with the above value. Hence, we can determine the heat of reaction from only E. M. F. measurements for all reactions for which suitable electric cells can be devised to carry out the reaction reversibly.

Notations and Conventions —For purpose of convenience we shall follow the notation of representing a cell by writing the chemical symbols of the electrodes and the chemicals in the cell starting with the negative electrode at the left hand side and ending with the positive electrode at the right extreme. For example, the Daniell cell would then be represented as—

$$Zn \text{ ; } ZnSO_4 \text{ || } CuSO_4 \text{ ; } Cu \qquad E = 1·05 \text{ volts.}$$
$$\longrightarrow$$
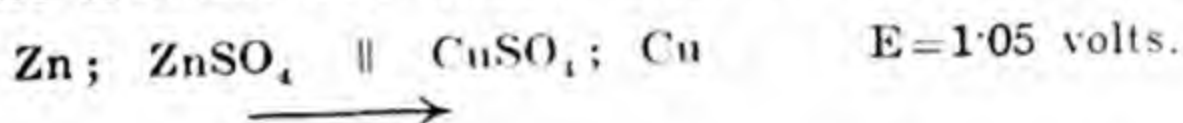
We can include the strength of the solutions by mentioning it within parenthesis following the symbol for the electrolyte. The double vertical line in the above scheme denotes the junction of the two liquids, the potential at their interface being generally eliminated or minimised by some suitable means as we shall see later. The arrow below denotes the direction of current *inside the cell*. Each half of the above cell is called a *half-cell*.

It should be made clear that we are perfectly justified to write the above cell also in the reverse way,

$$Cu \text{ ; } CuSO_4 \text{ || } ZnSO_4 \text{ ; } Zn \qquad E = -1·05 \text{ volts}$$
$$\longrightarrow$$
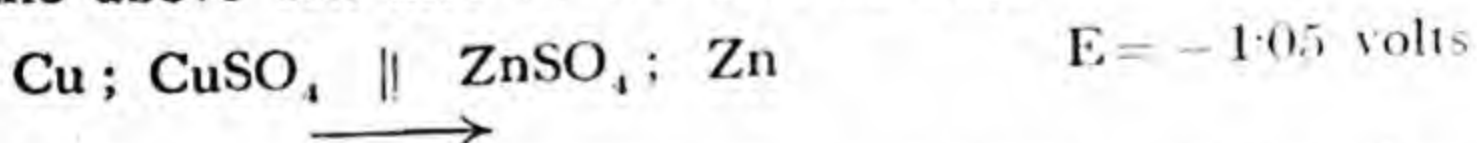
meaning that zinc is positive to copper to the extent of $-1·05$ volts. Hence the representation of an unknown cell will not introduce any difficulty and if we have done it in the reverse way, we shall come out on calculation with a negative value of the E.M.F. Since positive terms are easier to deal with and grasp, it is preferable to write the positive electrode on the right hand side whenever this information is available.

Various conventions are employed as to the sign as also the theoretical treatment of observed voltage, but the most simple

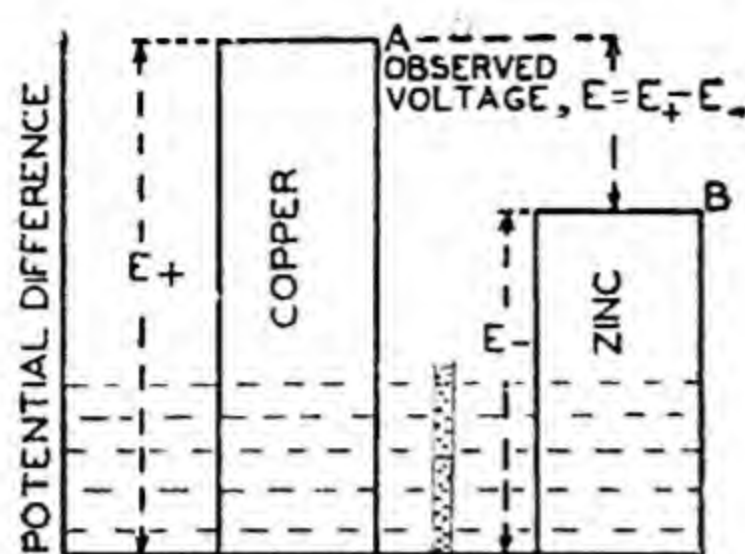and picturesque is to treat the observed voltage as shown in Fig. 96 with respect to the Daniell cell. The copper electrode has a potential E^+ (level A) above that of the solution and the zinc electrode has E_- (level B) above the same level and so the observed voltage, E is simply the difference between these two potentials (*i.e.* difference in level between A and B) as is clear from the figure. So, we have the equation,


Fig. 96—Observed Voltage as the Difference of two Potentials

$$E = E_+ - E_- \qquad \ldots \qquad \ldots \quad (4)\text{-XVIII}$$

The representation is merely conventional and we shall follow it consistently, and in effect it means that we are regarding all electrodes as positive with respect to the solution.

Suppose we add more copper ions to the copper side of the solution. The potential of the copper will naturally go up because we are adding the positive ion to the $Cu - Cu^{++}$ system (*vide eqn.* (6)-XVIII), and so the observed voltage will increase. On the other hand, if we introduce more zinc ions in the solution, the potential of the zinc electrode will of course similarly go higher up, but as can be easily seen from the figure, the observed potential will as a result decrease. This is obvious because if A (Fig. 96) goes up, the difference in level between A and B increases, whereas if B goes up, the same difference decreases. Any equation we arrive at for a cell must correctly answer the above test, *i.e.* an increase of c at the positive electrode with positive ions should increase the observed voltage and an increase of c at the negative electrode will decrease the observed voltage. *If negative ions are involved it will be just the reverse* [eqn. (13)]. The student should satisfy himself by checking all equations of this chapter with respect to this criterion. In fact if he masters the concept given in this para he can immediately write down the E. M. F. equation of any cell or half-cell at a glance of the composition of the cell. Hence, a correct understanding of this section can not be too strongly emphasised.

Thermodynamics of Reversible Cells, Nernst Equation— Let us calculate the E.M.F. of the following typical cell thermodynamically.

$$Zn \; ; \; ZnSO_4(c_1) \; \| \; CuSO_4(c_2) \; ; \; Cu$$
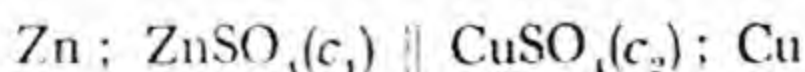
The cell reaction is $Cu^{++} + Zn = Cu + Zn$

According to eqn. (15)-XIV, we have for the free energy change, $\triangle F$, of this reaction the following relation—

$$\triangle F = \triangle F^\circ + RT \, ln \, \frac{[Zn^{++}] \times [Cu]}{]Cu^{++}] \times [Zn]}$$

Since the active mass of a solid is constant, we can include it with the constant term, $\triangle F^\circ$, the free energy change under standard conditions, and forget all about it. So, the above equation is equivalent to

$$\triangle F = \triangle F^\circ + \frac{RT}{nF} \, ln \, \frac{|Zn^{++}|}{|Cu^{++}|}$$

Putting $\triangle F = -nFE$, where E is the voltage of the cell [eqn. (2)] and for the sake of similarity $\triangle F^\circ = -nFE^\circ$, we have

$$E = E^\circ + \frac{RT}{nF} \, ln \, \frac{[Cu^{++}]}{[Zn^{++}]} \qquad \qquad \text{... (5)-XVIII}$$

We can go a step further and express $E = E_+ - E_-$ [eqn. (4)-XVIII] and similarly $E^\circ = E^\circ_{Cu} - E^\circ_{Zn}$; we thus obtain

$$E = E_+ - E_- = \left(E^\circ_{Cu} + \frac{RT}{nF} \, ln \, |Cu^{++}| \right) - \left(E^\circ_{Zn} + \frac{RT}{nF} \, ln \, [Zn^{++}] \right)$$

which, as is easily seen, can be separated into two equations,

$$E_+ = E^\circ_{Cu} + \frac{RT}{nF} \, ln \, [Cu^{++}] \text{ and } E_- = E^\circ_{Zn} + \frac{RT}{nF} \, ln \, [Zn^{++}]$$

Hence, for the general case of a metal of valency n in contact with its ions at a concentration c, we can express its potential E as

$$E = E^\circ + \frac{RT}{nF} \, ln \, c \qquad \qquad \text{...} \qquad \text{... (6)-XVIII}$$

which on substitution of the values of the constants and conversion in ordinary logarithm becomes at 25°C

$$E_+ = E^\circ + \frac{0.059}{n} \, log \, c \qquad \qquad \text{...} \qquad \text{... (7)-XVIII}$$

where E° is the standard electrode potential (reduction) of the electrode.

This equation is called Nernst equation and gives the potential of the electrode over the solution. Nernst derived this equation in 1882 by a different method but his derivation is seldom used nowadays, and the equation for a cell or a single electrode is directly derived from thermodynamic free energy equation as done here.

E. M. F. of a complete cell—So, to obtain the E.M.F of a reversible cell, the following simple rules may be set up.

    (i) *Write down the complete cell reaction.*

    (ii) *Write down the $\triangle F$ for it (equation (13)-XIV).*

    (iii) *Put $\triangle F = -nFE$, $\triangle F^\circ = -nFE^\circ$ and divide E° and the other terms on the right hand side into two parts to correspond with two half cell reactions.*

(iv) *Substitute $E°$ value from the table, taking care that $E°$ (oxidation)$=-E°$ (reduction).*

The above procedure will cover all types of cell reactions, and so we have in a sense learnt to treat all types of cell reactions on a common basis. This is examplified below by another example, *viz.* by the calculation of the E.M.F. of the following cell.

$$Ag \mid AgNO_3 \ (c) \parallel KCl, \ HgCl \ (s) \mid Hg$$

(i) We first write down the cell reaction as below, if current passes within the cell from left to right.
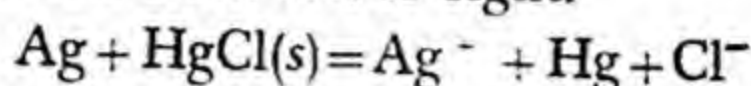
$$Ag + HgCl(s) = Ag^- + Hg + Cl^-$$

(ii) We next set up the free energy equation, *viz.*

$$\Delta F = \Delta F° + RT \, ln \, \frac{[Ag^-][Hg][Cl^-]}{[Ag][HgCl(s)]}$$

(iii) setting $\Delta F = -nFE$, $\Delta F° = -nFE°$, and the concentrations of all solids equal to unity, we obtain

$$E = E° - \frac{RT}{F} \, ln \, [Ag^+][Cl^-]$$

The $E°$ value can be divided into two parts, corresponding to the two half cells.

$$\therefore \ E = E°_{([Hg][Cl^-]/HgCl(s))} - \frac{RT}{F} \, ln \, [Cl^-]$$

$$+ E°_{(Ag+/Ag)} - \frac{RT}{F} \, ln \, [Ag^+]$$

Now $E°_{(Ag+/Ag)} = -E°_{(Ag/Ag+)}$

$$\therefore \ E = E°_{([Hg] \times [Cl^-]/HgCl(s))} - \frac{RT}{F} \, ln \, [Cl^-]$$

$$- [E°_{(Ag/Ag)} - \frac{RT}{F} \, ln \, (Ag^-)] \qquad \dots \ (8)\text{-XVIII}$$

The equation is correct with respect to sign as it checks up against the criterion set up in Fig. 96.

EXAMPLE 1. *Calculate the voltage at $25°C$ of a cell formed by dipping silver in silver nitrate (0·1 molal) and zinc in zinc sulphate (0·2 molal) and connecting them without junction potential.*

Writing the cell as $Ag : AgNO_3$ (0·1 M) $\mid ZnSO_4$ (0·2 M) ; Zn, we have the cell reaction, $2Ag + Zn^{++} = 2Ag^- + Zn$ and so the E.M.F. according to the procedure laid down in this section is

$$E = E°(Ag^+/Ag) - \frac{RT}{F} ln \, [Ag^-] + E° \, (Zn/Zn^{++}) + \frac{RT}{2F} \, ln \, [Zn^{++}]$$

$$= E°(Zn/Zn^{++}) + \frac{RT}{2F} \, ln \, [Zn^+] - E°(Ag/Ag^+) - \frac{RT}{F} \, ln \, [Ag^+]$$

$$= (-0·762 + 0·0295 \, log \, 2) - (0·798 + 0·059 \, log \, ·1) = -1·522 \text{ volts.}$$ So silver would be the positive electrode and the total E.M.F. is 1·522 volts. **Note** that it does not matter which cell is assumed positive; if we have not made the right choice the calculated E.M.F. would come out negative.

Thus with a table for $E°$ we are in a position with the help of the above procedure to calculate the E.M.F. of any reversible cell whatsoever.

Conventional Value for the Potential of a Halfcell—Though we are able to calculate the potential of any complete cell with the help of eqn. (8), there is no way of knowing the absolute value of the E. M. F. of a half-cell. However, we are very often interested in the behaviour of a half-cell, measured with respect to any arbitrary standard.

The *universal convention* has been adopted to regard *the potential of a hydrogen electrode at one atmospheric pressure in contact with a solution containing hydrogen ions at unit effective concentration to be zero*. Such a hydrogen electrode is called a *normal or standard hydrogen electrode* and is represented as H_2 (1 atm.) ; H+ (effective conc.$=1$), or Pt, H_2 (1 atm.) ; H$^-$ $(a=1)$, since hydrogen being a gas is generally adsorbed on platinised platinum electrode, and this combination behaves as an electrode of hydrogen.

We should point out here that a new term *effective concentration* has been introduced here. It has been found that a molal solution of say, hydrochloric acid does not contain H+ ion at unit concentration and hence a small correction is often necessary. To determine this correction is beyond the scope of the present book but for our purpose it is sufficient to know that all concentration terms used in this chapter are really *effective concentration*, or better known as *activity* (represented by a). However, the correction for dilute solutions is often small and henceforth, we shall neglect it.

With the above arbitrary standard, the E. M. F. of any electrode or half-cell is simply the potential of this electrode against a normal hydrogen electrode. Thus, the potential of a silver electrode according to this convention means the E. M. F. of the following cell—

$$\text{Pt, } H_2 ; \ H+(a=1) \parallel Ag^+ (c) ; \ Ag. \qquad E=0\cdot799 \text{ volts.}$$

$$\longrightarrow$$
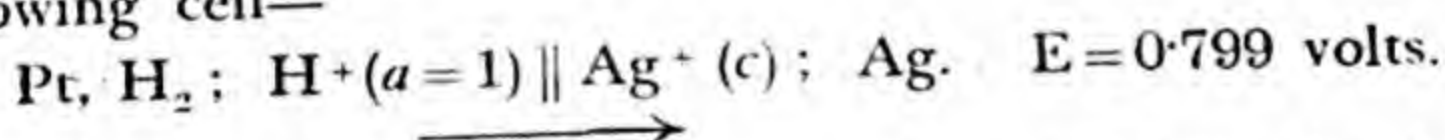
Note that we have written the above cell with the Ag electrode on the right indicating that we are measuring its potential against the hydrogen electrode.

The potential of the above electrode according to eqn. (8), however, is $E=E°_{(Ag/Ag^+)}+0\cdot059 \log C_{Ag}{}^+-(E°_{H_2}+0\cdot059 \log C_H{}^+)$ But, by the above convention $E°_{H_2}=0$ and also $C_H{}^+=1$ *i.e.*, $\log C_H{}^+=0$ and so we obtain,

$$E = E°_{(Ag/Ag^+)} + 0\cdot059 \log c_{Ag}{}^+$$

i.e. for the general case of any metal ion,

$$E = E° + \frac{\overline{RT}}{nF} \ln c \qquad \cdots \qquad \cdots \qquad \cdots \ (9)\text{-XVIII}$$

as the potential of any half-cell measured against the standard hydrogen electrode which is the same as that given by Nernst equation (eqn. (6)-**XVIII**).

Standard Electrode Potential—If in the above expression (eqn. (9)-XVIII) for the potential of a single electrode, we put $c=1$, we get $E=E°$. That is, if we measure the potential of the electrode at an effective concentration of unity of the reversible ion, we arrive at a potential characteristic of the electrode process. This potential is called the standard electrode potential of the particular electrode and is generally designated by $E°$.

Hence, *standard electrode potential*, $E°$ can be defined as *the potential of an electrode immersed in a solution of unit (effective) concentration of the reversible ion measured against a normal hydrogen electrode.* A better definition from theoretical standpoint would be to say that it is the potential associated with the conventional electrode process, where the ions are at unit effective concentration (activity). The electrode process is according to our convention,

$$M^+(a=1)+\epsilon = M \text{ or } M^{n+} +n\epsilon = M$$
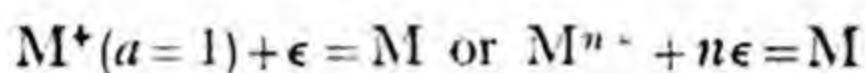
Since the above equation represents a reduction process, standard electrode potential, as defined above, is often called, for the sake of clarity, standard reduction potential. A few typical values of $E°$ are given in the following Table.

STANDARD ELECTRODE POTENTIALS, 25° (*Reduction*)

Electrode	Electrode reaction	E° (volts)
Pt, MnO$_4^-$, H	MnO$_4^-$+8H$^+$ + 5ϵ = Mn^{++}+4H$_2$O	1·52
Pt, Cl$_2$(g); Cl	$\frac{1}{2}$Cl$_2$ + ϵ = Cl$^-$	1·360
Au, Au	Au^{+++} + 3ϵ = Au	1·06
Hg, Hg$_2$	Hg$_2^{++}$ + 2ϵ = 2Hg	0·799
Ag, Ag	Ag$^+$ + ϵ = Ag	0·798
pt ; Fe^{+++}, Fe	Fe^{+++} + ϵ = Fe^{++}	0·771
Cu, Cu^{++}	Cu^{++} + 2ϵ = Cu	0·344
Calomel electrode	$\frac{1}{2}$Hg$_2$Cl$_2$ + ϵ = Hg+Cl$^-$	0·280
(Pt) H$_2$, H	H$^+$ + ϵ = $\frac{1}{2}$H$_2$	0·000
Pb, Pb^{++}	Pb^{++} + 2ϵ = Pb	−0·122
Sn, Sn^{++}	Sn^{++} + 2ϵ = Sn	−0·136
Zn, Zn^{++}	Zn^{++} + 2ϵ = Zn	−0·762
Mg, Mg^{++}	Mg^{++} + 2ϵ = Mg	−1·866
Na, Na$^+$	Na$^+$ + ϵ = Na	−2·715
Li, Li$^+$	Li$^+$ + ϵ = Li	−2·959

A few points need be noted in this connection. Many authors prefer to define the standard electrode potential with respect to the cell reaction at the negative electrode, *i.e.* to the oxidation process, $M = M^+(a=1)+\epsilon$. Evidently, the $E°$ values in their system will be negative of the corresponding values in our system. The $E°$ values in that system should be truly called standard oxidation potential. $\therefore$ $E°$ (reduction$= - E°$ (oxidation) ... (9a)

It should be further noted that according to the convention adopted in this book, our $E°$ values represent the actual E.M.F. of the cell with the given electrode against the standard hydrogen

electrode. From the table it will be seen that noble metals like gold, silver, copper, mercury, etc. have positive E° values showing that they are discharged when copuled with a normal hydrogen electrode. Metals like zinc, iron, sodium, etc. have negative values showing that they form the negative electrode when coupled with a hydrogen electrode and therefore, hydrogen is liberated by these metals from solutions containing hydrogen ions. In fact, any element standing higher in the standard reduction potential series will be liberated by another standing lower with respect to it and this is the reason why iron dissolves in copper sulphate solution liberating copper, or zinc dissolves in silver nitrate solution liberating silver. The standard electrode potential series for metals is also known as *Electromotive Series* for metals.

Thermodynamic Significance of E°—The thermodynamic significance of the E° values is simply that $nFE°$ is the decrease in free energy, $-\triangle F$ of reaction (i), or as *conventionally* written, of reaction (ii), as is also shown in the E° table.

(i) $M^+ (a=1) + \frac{1}{2}H_2 = M + H^+ (a=1)$;   (ii) $M^+ (a=1) + \epsilon = M$
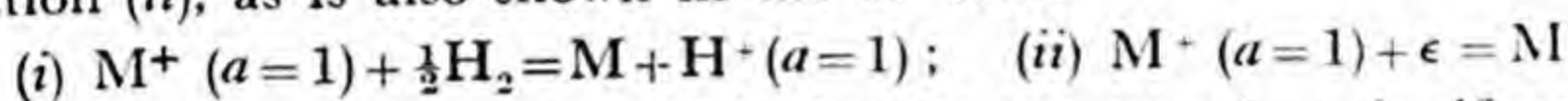
From thermodynamic standpoint E° has no other significance but above. It is a very important constant for any electrode process and is indispensable in many E. M. F. calculations.

EXAMPLE 2. *What will be the E. M. F. of a Daniell cell using zinc sulphate and copper sulphate solution at unit concentrations?*

$E = E°_+ - E°_-$, where $E°_+$ is for the reaction $Cu^{++} + 2e = Cu$ and $E°_-$ is for the reaction $Zn^{++} + 2e = Zn$. Now, $E°_+$ is the standard electrode potential for copper and $E°_-$ is the standard electrode potential for zinc, i.e.,

$$E = E_+ - E_- = E°_{Cu} - (E°_{Zn}) = 0.344 + 0.762 = 1.106 \text{ volts.}$$

Determination of Equilibrium Constant from E°-Values—Since $-\triangle F° = nFE°$ [eqn. (2)] and also $-\triangle F° = RT lnK$ [eqn. (16)-XIV], we have

$$nFE° = RT\, lnK \qquad\qquad ... \text{(10)-XVIII.}$$

Therefore, from the above equation we can calculate the equilibrium constant, K of any reaction provided the latter can be expressed as the net result or combination of two single electrode reactions as shown in the following example.

EXAMPLE 3. *If zinc is placed in a solution of copper sulphate, zinc dissolves and copper is deposited. Calculate how much copper will be left in solution if excess of zinc is present.*

The above is simply a calculation of the equilibrium constant of the reaction, $Cu^{++} + Zn \rightleftharpoons Cu + Zn^{++}$. The given reaction is the difference of two reduction reactions. (1) $Cu^{++} + 2\epsilon = Cu$, ($E° = 0.344$ volts) (2) $Zn^{++} + 2\epsilon = Zn$, ($E° = -0.762$ volts). Total $E° = E°_{cu} - E°_{zn} = 0.344 - (-0.762) = 1.106$ volts. ∴ $2F \times 1.106 = RT \times 2.303 \log K$ ∴ $\log K = 2 \times 1.106/0.059 = 37.5$. So, under usual conditions there will be practically no copper ions left in solution. Note that we have subtracted the two E° values because we have adopted the convention of expressing the total E. M. F. as a difference of two reduction potentials.

Calomel Electrode—Though the above convention employs hydrogen electrode as the *reference electrode,* for practical purpose, it is not convenient to use hydrogen electrode, and other reference electrodes which are more convenient to handle are used. The observed values are however always expressed in terms of the hydrogen electrode as calculated from the known value of the reference electrode against the hydrogen electrode. The most commonly used reference electrode is known as the calomel electrode.

This half-cell is a mercury-mercurous chloride electrode in contact with a potassium chloride solution saturated with mercurous chloride. The strength of the potassium chloride solution may be varied and the more common ones contain either decinormal, normal or saturated solutions of KCl and are designated as such. Vessels of various shapes and designs are used and a common form coupled with a hydrogen electrode is shown in Fig. 97. The E.M.F. of a decinormal calomel electrode is 0·333 volts at 25°C.

Classification of Electrodes—Various types of electrodes are used of which we shall study only the following types—

(*i*) Metal-metal ion electrode including concentration cells.

(*ii*) Metal-insoluble salt electrode.

(*iii*) Gas electrode *e.g.,* Hydrogen electrode.

(*iv*) Oxidation-reduction electrodes (Redox potential).

Metal-Metal Ion Electrode —Whenever a metal is dipped in a solution containing its ions, there is a potential difference established at the junction between the metal and the solution. If the metal is the positive electrode, the conventional equation for the electrode reaction is $M^{n+} + n\epsilon - M$, and therefore by following the procedure of equation (8), we obtain

$$E = E^\circ + \frac{0.059}{n}\log c$$

where E° is the standard electrode potential (reduction) of the metal of valency n and c is the concentration of the metal ions.

The student should very carefully keep in mind the notation and convention we are using with respect to the above equation. In the above equation, E° is the *standard reduction potential,* corresponding to the reaction, $M^+ + \epsilon = M$. Therefore, the above equation gives the potential of an electrode over the solution (*vide* Fig. 96).

Let us now apply it to a specific example, say, the following cell.

$$Zn : ZnSO_4 \text{ soln. } \| \text{ AgNO}_3 \text{ soln}; \text{ Ag}$$
$$\longrightarrow$$
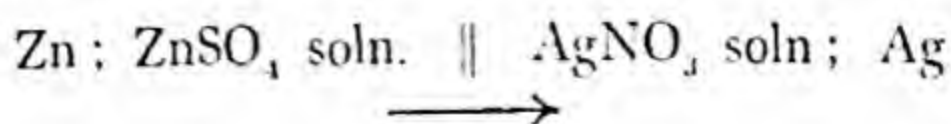
We have, using our notation and procedure (eqn. (8) and Example 1),

$$E = E^\circ{}_{Ag} - E^\circ{}_{Zn} + 0.059 \log \frac{[Ag^+]}{\sqrt{[Zn^{++}]}} \qquad \ldots (11)\text{-XVIII}$$

Hence knowing the concentration of silver ions and zinc ions and the standard electrode potentials of silver and zinc we can calculate the E.M.F. of the above cell.
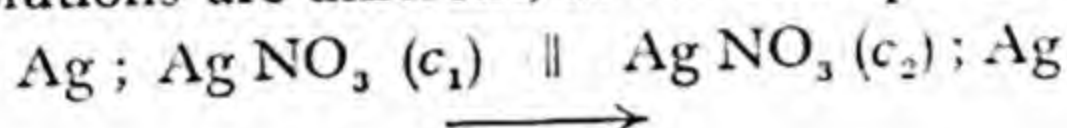
Similarly, if we have the Daniell cell,

$$Zn \; ; \; ZnSO_4 \text{ soln} \parallel CuSO_4 \text{ soln} ; \; Cu$$
$$\longrightarrow$$
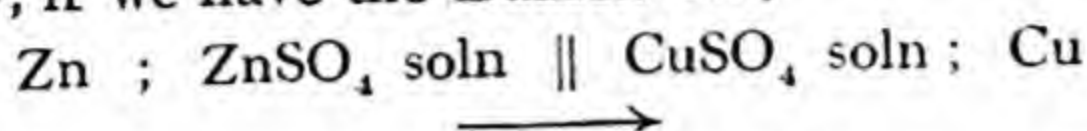
We can immediately write out the E.M.F. of the cell, E at 25°

$$E = E^\circ{}_{Cu} - E^\circ{}_{Zn} + \frac{0.059}{2} \log \frac{[Cu^{++}]}{[Zn^{++}]} \qquad \ldots (11a)\text{-XVIII}$$

Concentration Cell—A very interesting situation arises if both the electrodes are of the same metal but the concentrations of the two solutions are different, as for example in the cell—

$$Ag \; ; \; AgNO_3 \; (c_1) \parallel AgNO_3 \; (c_2) ; \; Ag$$
$$\longrightarrow$$

Here, the cell reaction is $Ag^+(c_1) = Ag^+(c_2)$

$$\therefore \qquad E = 0.059 \log \frac{c_2}{c_1} \qquad \ldots \qquad \ldots (12)\text{-XVIII}$$

i.e., the E.M.F. depends on the *relative concentration* of the reversible ion at the two electrodes and its valency. If c_2/c_1 is 10, the observed E. M. F. will be 0.059 volts, i.e., if we have say, a decinormal silver nitrate solution at the right hand electrode and a centinormal solution at the left hand electrode the observed E. M. F. of the cell will be 59 millivolts at 25°C.

Metal-Insoluble Salt Electrode—A good example is an electrode, formed by coating silver with silver chloride dipped in a solution of a chloride, i.e., the half-cell,

$$\parallel Cl^-(c), \; AgCl; \; Ag$$
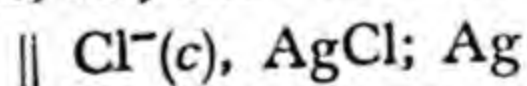
Here the half-cell reaction is $AgCl + \epsilon = Ag + Cl^-$ and so

$$\Delta F = \Delta F^\circ + RT \, ln \frac{[Ag] \times [Cl^-]}{[AgCl] \, [e]}$$

Now $\Delta F = -nFE$ and $\Delta F^\circ = -nFE^\circ$ and dropping out $[Ag]$, $[AgCl]$ and $[\epsilon]$ which are constants, we have $nFE = nFE^\circ - RT \, ln \, [Cl^-]$,

$$\text{or, } E = E^\circ - 0.059 \log [Cl^-]$$

where E° is the S.E.P. for the reaction $AgCl + e = Ag + Cl^-$.

This equation is just what is expected from the criterion set up on P. 284. If we increase the Cl^- ion concentration the potential will go down at the positive electrode as opposed to the copper of

19

the Daniell cell, because Cl⁻ is negative whereas Cu^{++} ion is positive. In the above equation an increase of [Cl⁻] leads to a decrease of E and therefore the equation is correct. So, we arrive at the important result that for an electrode reversible with respect to a negative ion, the electrode potential is

$$E = E° - \frac{RT}{nF} \, ln \, c \qquad \dots \qquad \dots \quad (13)\text{-XVIII}$$

where c is the conc. of the reversible negative ion and $E°$ is the S.E.P. (reduction) of the cell reaction. Note carefully that the negative sign in eqn. (13) as opposed to the positive sign in eqn. (6) comes from the fact that in the reduction process involving a negative ion, the ion appears on the right hand side (for example, $Cl + e = Cl⁻$) whereas in the reduction of a positive ion the ion appears on the left hand side (for example, $Ag⁺ + e = Ag$).

For the complete cell,

$$Ag \, ; Ag \, I, \, I⁻(c_2) \, \| \, Ag⁺(c_1); \, Ag$$

$$\overrightarrow{}$$
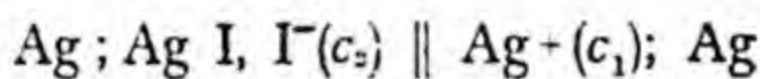
$$E_+ = E°_{Ag}⁺ + 0.059 \, \log \, [Ag⁺]$$

$$\text{and } E_- = E°_{(Ag; \, AgI, \, I⁻)} - 0.059 \, \log \, [I⁻]$$

$$E = E_+ - E_- = E°_{Ag} - E°_{(Ag; \, AgI, \, I⁻)} + 0.059 \, \log \, [Ag⁺] \, [I⁻] \dots (14)$$

Hydrogen Electrode —Just as a metal in contact with a solution containing its ions forms an electrode with a definite potential given by the Nernst equation, similarly any gas shows a potential with respect to a solution containing its ions. However, to make a steady contact and accurate measurement, the gas is adsorbed in platinised platinum which is kept dipped in a solution and serves as a gas electrode. The most important type of such a gas electrode is the hydrogen electrode.

$$(Pt) \, H_2 : H \, (a=1) \, \| \, [H⁺] : H_2(Pt) \qquad E = 0.059 \, \log \, [H⁺]$$

Since the cell reaction is $H⁺ \, (a=1) = [H⁺]$ the potential, E of such an electrode in contact with a solution whose hydrogen ion concentration is [H⁻] is.

$$E = E°_{H_2} + 0.059 \, \log \, [H⁺] \qquad \dots \qquad (15)\text{-XVIII}$$

Since by convention $E°_{H_2}$ is zero, we have

$$E = 0.059 \, \log \, [H⁺] \qquad \dots \qquad (16)\text{-XVIII}$$

Hence, if we measure the electrode potential of the above cell, we can calculate [H⁺] of the unknown solution. This is done by coupling the hydrogen electrode with a calomel half-cell. The hydrogen electrode in the unknown solution is often the negative electrode in the assembly since calomel is usually employed in such measurements, which is generally positive with respect to the hydrogen electrode. Thus, the observed E.M.F., E of the following set-up is as follows.

$$\text{Pt, } H_2 \text{ ; } [H^+] \parallel (N) \text{ calomel electrode}$$

$$E = E_+ - E_- = E \text{ (calomel)} - E \text{ (}H_2 \text{ electrode)}$$

$$= E \text{ cal.} - 0.059 \log [H^+]$$

$$= 0.281 - 0.059 \log [H^+] \qquad \ldots \text{ (17)-XVIII}$$

$$\therefore \quad -\log[H^+] = \frac{E - 0.281}{0.059} \qquad \ldots \qquad \ldots \text{ (18)-XVIII}$$

Therefore, by definition of $pH = -\log [H^+]$ (see next chapter) we have

$$pH = \frac{E - E \text{ calomel}}{0.059} = \frac{E - 0.281}{0.059} \qquad \ldots \text{ (19)-XVIII.}$$

This equation will be used in the experimental determination of pH as will be shortly explained in the next chapter.

Redox Potential —If we have a bright platinum in contact with a solution containing a reduced and an oxidised form, either or both of which are ions, we have got a half-cell which is very often reversible. Thus, for the half-cell,

$$\parallel Fe^{++}, Fe^{+++} | Pt$$
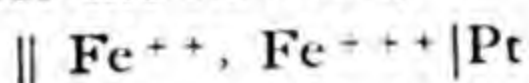
the cell reaction against a standard hydrogen electrode is $\frac{1}{2}H_2 + Fe^{+++} = Fe^{++} + H^+$, which may conventionally written as
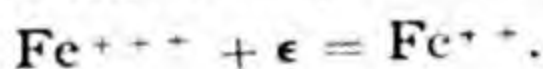
$$Fe^{+++} + \epsilon = Fe^{++}.$$

and so, the E.M.F. of the cell is, following our usual thermodynamic procedure according to equation (8)

$$E = E^°_{(Fe^{++}/Fe^{+++})} + \frac{RT}{F} ln \frac{Fe^{+++}}{Fe^{++}} \qquad \ldots \text{ (20)-XVIII}$$

where $E^°_{(Fe^{++}/Fe^{+++})}$ is the S.E.P. (reduction) i.e. S.E.P. of the reaction, $Fe^{+++} + \epsilon = Fe^{++}$.

It should be realised now that all the preceding equations for E.M.F. are special cases of this equation which can be put in the general form,

$$E = E^° \frac{\text{(Reduced form)}}{\text{(oxidised form)}} + \frac{RT}{F} ln \frac{[\text{oxidised form}]}{[\text{reduced form}]} \qquad \ldots \text{ (21)-XVIII.}$$

$$\text{or } E = E^°_{(red./ox.)} + \frac{RT}{nF} ln \frac{ox.}{red}$$

where $E^°_{(red./ox.)}$ is the standard electrode potential for the reduction process (S.E.P., reduction i.e. redox potential).

It can be easily shown from the above equation that any redox system with higher S.E.P. (reduction) i.e. higher $E^°$ (red./ox.) will oxidise any other with lower $E^°$ (red./ox.) . Thus, permanganate will oxidise ferrous iron because its $E^°$ is 1.52 volts as against $E^°_{Fe^{++}/Fe^{+++}}$ which is only 0.771 volts (vide Table); for similar reasons ferric salts can decolorise those dyes whose $E^°$ is

lower than that of ferrous/ferric system. Redox potentials are of great importance for biochemistry because living matter is full of redox reactions. It should be also realised that any redox reaction involves electrons, and so, the oxidation of one redox system by another is essentially an electron-transfer reaction, the electrons being transferred to the oxidant system from the oxidised. So, E° is a measure of the electron affinity of a system in solution.

Applications of E.M.F. Measurements—There are various important applications of E.M.F. measurements of reversible cells, some of which are listed below.

(1) Measurement of pH with the help of hydrogen electrode, quinhydrone electrode, glass electrode, etc.

(2) Measurement of ionic concentration and so the hydrolysis or solubility of a salt.

(3) Potentiometric Titrations, for example, the titration of Cl^- ion against Ag^+ by using a Ag-AgCl electrode, etc.

(4) Measurement of transport number of ions.

Since the E.M.F. contains a concentration (activity) term, any ion concentration can be measured if a cell reversible to the ion can be devised and practically all applications are based on this principle. The determination of pH and potentiometric titration will be dealt with in the next chapter.

Electrochemical Protection of Metals—From the table of standard electrode potentials it is easily seen that if we have two metals in contact, the nobler (*i.e.*, the more positive) one will not be in the least affected by say, an acid, as long as the less noble one remains in contact. For example, if iron is in contact with zinc, the zinc will dissolve prior to iron. Advantage is taken of this fact in protecting iron from corrosion by galvanising it with zinc. This simple idea, though basically sound, loses some of its force due to the existence of other factors, mainly irreversible electrode phenomena *e.g.* overvoltage, etc.

However, an outstanding example of the application of this principle is the modern method of cathodic protection of pipe lines. Hundreds of miles of pipe lines are laid to carry petroleum from the mine to the refineries, from refinery to port, etc. Such lines would be corroded out very soon and this is prevented by using *buried electrodes* for electrochemical protection, *i.e.* at intervals blocks of magnesium in electrical contact with the pipe line are buried along the route and a small current passed so that magnesium is the anode and the pipe is the cathode. Magnesium is preferentially corroded and is replaced from time to time thus prolonging the life of the expensive pipe line. Thus, magnesium is called the *sacrificial electrode* and the method is called cathodic protection. City water supply mains are sometimes also similarly protected.
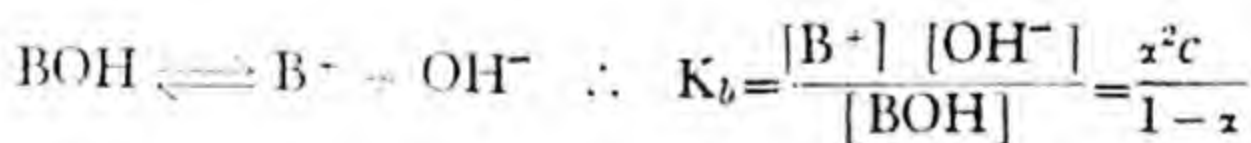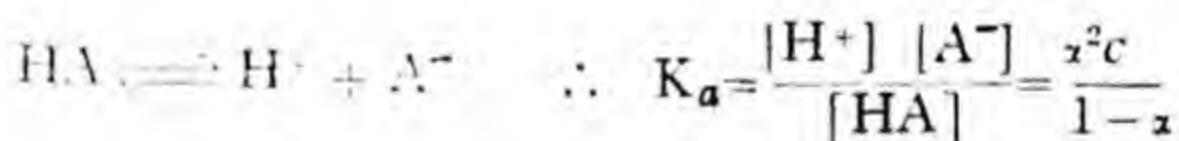
Exercise

1. Write notes on :—(a) reversible cells (b) buried electrode for protection (c) calomel electrode and (d) concentration cell.

2. Define standard electrode potential of an electrode and clearly distinguish S. E. P. (reduction) and S. E. P. (oxidation). Discuss the importance of such values in physicochemical calculations.

3. If a reversible galvanic cell is kept immersed in a tank of water and is allowed to send out current reversibly, how will the temperature of the tank be affected? Discuss thoroughly the theoretical principle on which your answer is based.

4. If in the previous example the whole cell with the wire carrying the current be kept immersed in the tank of water, what difference would you observe?

5. Deduce Nernst equation for the potential of a reversible (a) oxygen electrode, (b) electrode where the half-cell reaction is $N_2 + 2H_2O + \epsilon = NH_3 + \frac{1}{2}H_2 + NO_2^-$ and (c) a cell whose net result is the formation of $MgBr_2$ in solution.

CHAPTER XIX

ACIDS AND BASES; pH AND INDICATORS

The Classical Concept of Acids and Bases and their Dissociation Constants—The classical definition of acids as substances containing hydrogen ions replaceable by metals and having such properties as sour taste, corrosive action, causing colour change of indicators, etc., is, qualitatively speaking quite a sound one, but difficulties arise as soon as we attempt to arrive at a quantitative measure of the strength of acids on such basis. However, all acids in aqueous solution increase the H^+ ion concentration of water, and all bases decrease the same (and therefore increase the OH^- ion concentration) and so, a quantitative measure of acidity may well depend on this property of acids and bases.

Since the H^+ ion concentration (to be designated by $[H^+]$ or C_{H^+}) is simply related to the dissociation constant of Ostwald's dilution law (*vide* P. 259) we can aptly compare the strength of acids and bases by their dissociation constants, K_a and K_b respectively.

$$HA \rightleftharpoons H^+ + A^- \qquad \therefore \quad K_a = \frac{[H^+]\,[A^-]}{[HA]} = \frac{x^2 c}{1-x}$$

$$BOH \rightleftharpoons B^+ + OH^- \qquad \therefore \quad K_b = \frac{[B^+]\,[OH^-]}{[BOH]} = \frac{x^2 c}{1-x}$$

The above equations are applicable only to weak acids and bases and not to strong acids and bases, the latter being strong electrolytes (P. 261), and so, we can have K_a and K_b values for weak acids and bases only. It should be realised that by comparing K_a (and K_b) we are in a sense comparing their conductivities because the dissociation constants are usually determined from conductivity measurements (P. 260).

In the following table are compiled the values of K (*dissociation constants*) for many weak acids (and bases) arranged in decreasing order of strengths, which bring out clearly how greatly the acids and bases, which we class as weak differ amongst themselves in strength.

| Weak Acids	K_a	Weak Acids (contd.)	K_a
Dichloracetic acid	$5\cdot2 \times 10^{-2}$	Propionic ...	$1\cdot32 \times 10^{-5}$
Oxalic ...	$3\cdot8 \times 10^{-2}$	Carbonic ...	$3\cdot1 \times 10^{-7}$
Sulphurous	$1\cdot7 \times 10^{-2}$	Hydrogen Sulphide	$8\cdot0 \times 10^{-8}$
Maleic ...	$1\cdot2 \times 10^{-2}$	Hydrocyanic ...	$1\cdot3 \times 10^{-9}$
Phosphoric	$7\cdot6 \times 10^{-3}$	Boric ...	$6\cdot0 \times 10^{-10}$
Cyanoacetic	$3\cdot7 \times 10^{-3}$	Phenol ...	$1\cdot3 \times 10^{-10}$
Malonic	$1\cdot6 \times 10^{-3}$	Hydrogen Peroxide	$2\cdot0 \times 10^{-12}$
Monochloracetic	$1\cdot55 \times 10^{-3}$		
Salicylic	$1\cdot0 \times 10^{-3}$	Weak Bases	K_b
Hydrofluoric	$9\cdot0 \times 10^{-4}$		
Citric ...	$8\cdot0 \times 10^{-4}$	Diethylamine ...	$1\cdot26 \times 10^{-3}$
Nitrous ...	$6\cdot0 \times 10^{-4}$	Dimethylamine	$5\cdot0 \times 10^{-4}$
Formic ...	$2\cdot0 \times 10^{-4}$	Ethylamine ...	$4\cdot6 \times 10^{-4}$
Cyanic ...	$1\cdot5 \times 10^{-4}$	Methylamine ...	$4\cdot0 \times 10^{-4}$
Lactic ...	$1\cdot3 \times 10^{-4}$	Trimethylamine	$6\cdot5 \times 10^{-5}$
Succinic ...	$6\cdot7 \times 10^{-5}$	Ammonia ...	$1\cdot8 \times 10^{-5}$
Benzoic ...	$6\cdot1 \times 10^{-5}$	Hydrazine ...	$2\cdot2 \times 10^{-6}$
Acetic ...	$1\cdot8 \times 10^{-5}$	Pyridine ...	$2\cdot3 \times 10^{-9}$
Butyric ...	$1\cdot5 \times 10^{-5}$	Aniline ...	$5\cdot0 \times 10^{-10}$
		Urea ...	$1\cdot5 \times 10^{-14}$

Remarks on Strength of Organic Acids—It should be pointed out from the table that the strength of an acid increases by the replacement of hydrogen by electro-negative (electron-attracting) radicals e.g. Cl,CN, etc. in the anion of the acid because this makes the $-COO^-$ end more positive and so more repelling to the hydrogen ion. Thus, in the series, acetic, monochloracetic, dichloracetic and trichloracetic acids, the strength rapidly increases in the above order, and in fact, trichloracetic acid is almost as strong as nitric acid. Similar remarks also apply to the series acetic, monofluoro, difluoro and trifluoro acetic

Acid	K_a	Acid	K_a
CH_3COOH	2×10^{-5}	CH_3COOH	2×10^{-5}
$ClCH_2COOH$	155×10^{-5}	FCH_2COOH	210×10^{-5}
$Cl_2CHCOOH$	$5,200 \times 10^{-5}$	$F_2CHCOOH$	303×10^{-5}
$Cl_3C\ COOH$	$20,000 \times 10^{-5}$	F_3CCOOH	$5,880 \times 10^{-5}$

acids. It should be also observed that carbonic acid is much stronger than hydrocyanic acid, which is the reason of KCN getting converted into K_2CO_3 on long exposure to air. Carbolic acid is also weaker than carbon dioxide (carbonic acid) and so on passing CO_2 through sodium salt of carbolic acid ($C_6H_5O\ Na$), the free carbolic acid is precipitated ; conversely, phenol dissolves in NaOH but not in Na_2CO_3.

Strength of Inorganic Acids—The inorganic acids which appear to be very strong have gradation in acid strength among

themselves. The order of acid strength of the strong acids is roughly as follows:

$$HClO_4 > HI > HBr > HNO_3 > HCl > H_2SO_4 > H_3PO_4.$$
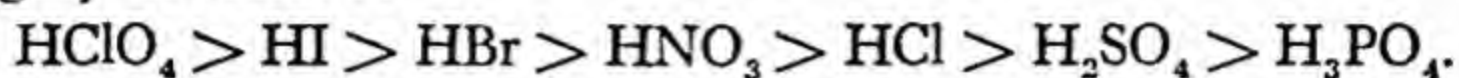
In oxygenated acids of similar structure the more electro-negative (electron-attracting) is the central atom, the stronger becomes the acid. This is shown in the table below for the S, Se and Te series as also for the Cl, Br and I series by a comparison of strength of acids of similar structure. This behaviour is caused by the same reason as increases the acid strength of an

Acid	First Ionisation Const., K_{a_1}	Acid	K_a
H_2SO_3	... 1.7×10^{-2}	HOCl	... 3.5×10^{-8}
H_2SeO_3	... 3×10^{-3}	HOBr	... 2×10^{-9}
H_2TeO_3	... 6×10^{-6}	HOI	... 5×10^{-13}

organic acid by the introduction of a negative group. This also explains why sulphuric acid is stronger than sulphurous acid or for that matter a higher oxygenated acid than the corresponding less oxygenated acid, because the central atom has a more formal positive charge i.e. is more electron-attracting in the former case. The strength of the hydrogen halide acids however, is in the reverse direction, viz. $HI > HBr > HCl$ because as the halogen atom becomes larger, the charge density becomes smaller and so it becomes easier for the hydrogen ion to escape from the negative halide ion.

Remarks on the Strength of Bases —As regards the strength of organic bases, diethyl amine and guanidine are among the strongest ones. It is of interest to note that in the series ammonia, methylamine, dimethylamine and trimethylamine as also in the series ammonia, ethylamine, diethylamine and triethylamine, the strength increases continuously up to the secondary amine and then it suddenly drops steeply on passing from the secondary to the tertiary amine. It seems as if the crowding of the three alkyl groups round the nitrogen atom somehow screens its lone pair of electron responsible for its basic power (probably by steric hindrance or some other less understood mechanism). Also, it is of interest to observe that aniline and pyridine are extremely weak in comparison with ammonia, and diethylamine is the strongest among alkyl and arylamines.

Other Methods of Determining Acid Strength —Strong acids, however, do not admit of measurement of their dissociation constants. So, their strengths are often compared by distribution of one base between two acids. For example, if the strengths of hydrochloric and meta-phosphoric acids are to be compared, we have simply to determine the point of equilibrium in the following system—

$$NaPO_3 + HCl \rightleftharpoons NaCl + HPO_3.$$
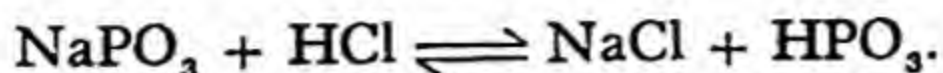
If the hydrochloric acid is the stronger of the two, the equilibrium will be more towards the right.

No method of chemical analysis is suitable for the analysis of the system, since it will disturb the equilibrium point. *Physical methods*, which require the measurement of variation of some physical property of the system, which changes with the composition of the system are usually resorted to. The physical properties largely used are *heat of reaction* by Thomsen and the *change of volume* by Ostwald, though other properties, viz. refractive index, etc. have also been used. The relative strength thus obtained is called *avidity ratio*, and is independent of the nature of the base competed for, which shows that *the avidity is a specific property of the acid.*

THOMSEN'S THERMOCHEMICAL METHOD. EXAMPLE 1. *Heats of neutralisation of sulphuric and hydrochloric acids by caustic soda are 15,650 and 13,700 calories respectively. On the addition of 1 equivalent sulphuric acid to 1 equivalent sodium chloride, the heat evolved is 350 calories. Calculate the avidity ratio.*

If the reaction, $\frac{1}{2}H_2SO_4 + NaCl \longrightarrow \frac{1}{2}Na_2SO_4 + HCl$ goes to completion, the heat evolved $= 15,650 - 13,700 = 1950$ calories. The observed amount of heat $= 650$ calories. $\therefore$ The displacement of HCl is only $650/1950 \times 100 = 33\%$. $\therefore$ Strength of HCl : Strength of $H_2SO_4 = 67 : 33 = 2 : 1$.

OSTWALD'S VOLUME METHOD. EXAMPLE 2. *The volume increment in the neutralisation of nitric and dichloro-acetic acids by caustic potash are 20 and 13 c.c. respectively. In the reaction between potassium-dichloracetate and nitric acid, the observed increase of volume is 5·67 c.c. Calculate the relative strength of the acids.*

(a) $HNO_3 + KOH \longrightarrow KNO_3 + H_2O$; volume increase $= 20$ c.c.

(b) $CHCl_2COOH + KOH \longrightarrow CHCl_2COOK + H_2O$ $= 13$ c.c

(c) $CHCl_2COOK + HNO_3 \rightleftharpoons CHCl_2COOH + KNO_3.$

If reaction (c) were complete, it would be accompanied by $20 - 13 = 7$ c.c. increase in volume; for, the above reaction may be regarded as the sum of the reverse of reaction (b) and direct reaction (a). But the actual increase is only 5·67 c.c. ; therefore the reaction has gone towards the right to the extent of $(5·67/7) = 80$ per cent approximately. Therefore the relative strength or avidity ratio of these two acids is in the ratio 80 : 20 or 4 : 1.

Catalytic Power of Acids and Bases—The strength of acids may also be compared by their ability to accelerate the rate of certain chemical reactions, notably the inversion of cane sugar and the hydrolysis of methyl acetate. The most important result of such determination is that the *order of strength of different acids* obtained by this method is *the same as that obtained by the previous methods,* and in fact a rough measure of the $[H^+]$ of an acid solution and so its dissociation constant may thus be obtained. The strength of bases may as well be determined by similar methods.

Modern Concept of Acids and Bases—The classical definitions of acids and bases assigning all-important position to hydrogen

and hydroxyl ions are useful and adequate for aqueous solutions but difficulties arise as soon as attempts are made to apply them to non-aqueous solutions. For example, sodamide ($NaNH_2$) when dissolved in liquid ammonia has properties analogous to caustic soda in water; besides being completely dissociated it has the capacity to neutralise an acid and can turn phenolphthalein pink. It can also precipitate heavy metals as amides just as hydroxides are precipitated by NaOH in water. Hence, there is no denying that sodamide is a strong base in liquid ammonia.

According to the newer concept of Brönsted and Lowry (1923) the acidic property is as usual associated with the hydrogen ion or proton, but the whole mechanism of acidity in solution is ascribed to a combination of the H^+ ion with a molecule of the solvent. In other words, whenever an acid is dissolved in a solvent the hydrogen ions or protons being incapable of separate existence, get solvated by the solvent molecules and remain only as a solvated unit. Thus, in water hydrogen ions remain as H_3O^+ (oxonium ion also called hydronium ion), in liquid ammonia as in glacial acetic acid as $CH_3COOH_2^+$ and so on. The extent of acidity depends on the extent to which the solvolysis goes from left to right as shown below for hydrochloric acid is aqueous solution—

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
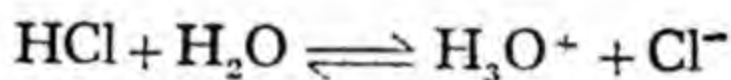
In case a solvent is a poor acceptor for protons, this reaction will go very little to the right and the acid will then be weakly dissociated. This actually happens in glacial acetic acid medium where hydrochloric acid is a rather weak acid. Hence we arrive at two very important conclusions about acids—

(i) *Acids are substances which can donate protons,*

(ii) *The strength of an acid will depend on the capacity of the solvent for acceptance of the proton.*

The fruitfulness of the above idea is at once evident when the so-called strong acids, HCl, HNO_3, H_2SO_4, $HClO_4$, etc. are dissolved in a solvent like acetic acid, which is a poor acceptor for protons. It is observed that though they are of practically equal strength in water all these acids behave like comparatively weak acids of unequal strengths under such conditions, and their strengths can be compared in this solvent.

An extreme case is supplied by solvents like liquid HF which have not the least power to accept protons. Here, even strong acids like nitric acid will not be able to manifest acidic properties, as no transfer of proton from the acid to the solvent is possible. In fact, the transfer of proton takes place the reverse way from the solvent to the nitric acid [*vide* eqn. (i)]. Now, if we compare this reaction with what takes place when ammonia is dissolved in water [eqn. (ii)], we find an exact analogy.

(i) $HNO_3 + HF \longrightarrow H_2NO_3^+ + F^-$

(ii) $NH_3 + HOH \longrightarrow NH_4^+ + OH^-$
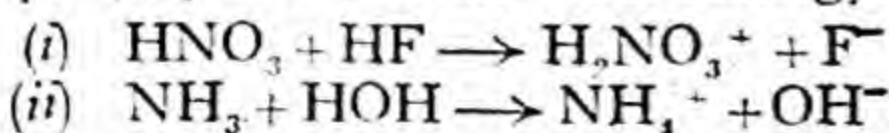
Hence we have as much reason to call ammonia and OH^- ions as bases, as we have to call here nitric acid and fluoride ions as bases. Thus, we come to a very important result that the anions of all acids are bases and that even a typical strong acid like nitric acid may function as a base in a suitable solvent.

Definition of a Base—Hence, we formally define *a base as a substance which is capable of combining with a proton.*

Evidently, since acids donate protons and bases receive them, acids and bases must be mutually related by the following equation, where the acid and the corresponding base are said to be *conjugate* to each other.

$$HA \iff H^+ + A^-$$
$$\text{acid} \qquad \text{proton} \quad \text{base}$$
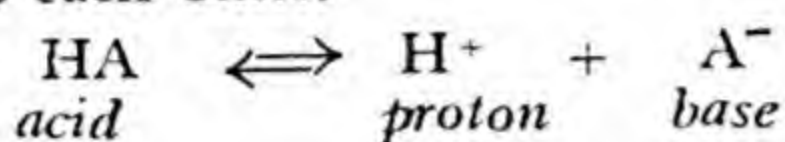
Accordingly, acetate ion, cyanide ion, free ammonia, etc. are all bases since they have the power to combine with a proton to form the conjugate acids, CH_3COOH, HCN, NH_4^+, etc. We should rather call the hydroxyl ion as the base instead of designating caustic soda by such name.

The new concept provides a simple method of viewing the hydrolysis of salts. As indicated in the previous para, the acetate ion is a base of considerable strength because the equilibrium,

$$CH_3COO^- + H^+ \iff CH_3COOH$$
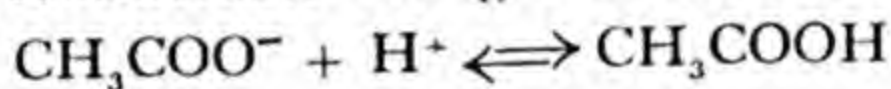
lies quite close to the right hand side. Hence, a solution of sodium acetate would be basic because the solution would contain a large concentration of the base, the acetate ion. This is theoretically much simpler and more elegant than the classical method of treating such phenomenon (*see* end of last chapter).

Suppose we dissolve a very weak base say, aniline, in glacial acetic acid. The following solvolytic reaction will immediately take place practically to completion.

$$C_6H_5NH_2 + CH_3COOH \longrightarrow C_6H_5NH_3^+ + CH_3COO^- \text{ (base)}$$
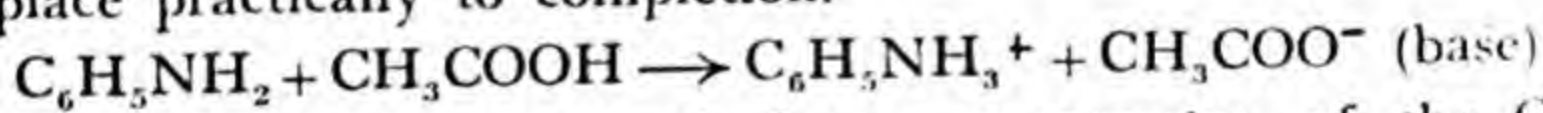
This will liberate an equivalent concentration of the CH_3COO^- ion, which, according to our definition, is a fairly strong base and so, the solution will be a strongly basic one. In fact, aniline and other very weak bases like pyridine etc., which are impossible to be titrated in aqueous solution with any degree of accuracy, are easily titrated in glacial acetic acid solution. In a solvent like hexane, benzene, etc. which is capable of neither donating nor accepting protons, a substance will be neither basic nor acidic but nevertheless, such solvents may also serve as media for neutralisation reactions.

Types of solvents—According to this new concept the development of acidic and basic property depends on the type of solvent and in the above discussion we have roughly classified them into three divisions. (1) Solvents which can take up proton *e.g.* H_2O, NH_3, etc. called basic or PROTOPHILIC solvents; (2) solvents which can donate protons *e.g.*, H_2O, HF, etc. called acidic or PROTOGENIC solvents, and (3) solvents which cannot participate in proton transfer, *e.g.* hexane, benzene, etc. called

inert or APROPTIC solvents. Water, alcohol, etc. which can both donate and accept protons are called AMPHIPROTIC solvents.

Amphoteric Electrolytes or Ampholytes—*An amphoteric substance is one which in solution can give rise to both hydrogen and hydroxyl ions, i.e.* it can behave both as an acid and as a base. Common examples of *ampholytes* are $Zn(OH)_2$, $Al(OH)_3$, etc. $Zn(OH)_2$ may be supposed to be capable of ionising in two ways,

(1) $Zn(OH)_2 \Longleftrightarrow Zn^{++} + 2(OH)^-$

or,   (2) $Zn(OH)_2 \Longleftrightarrow 2H^+ + ZnO_2^{--}$
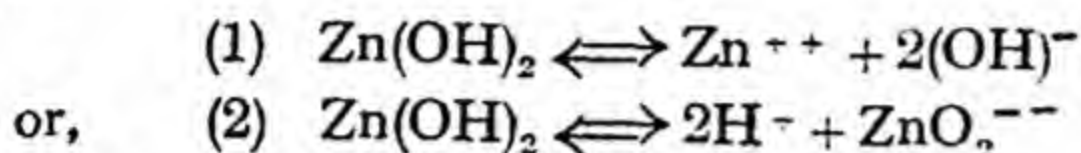
Acids favour the first type of ionisation by removal of OH^- whereas alkalies favour the second type of ionisation by removal of H^+ ions. So, an acid solution of $Zn(OH)_2$ contains Zn^{++} ions which migrate on electrolysis towards the cathode; alkaline solution contains zincate (ZnO_2^{--}) ions which travel on electrolysis towards the anode. Such electrolytes are called ampholytes.

Amino-acetic acid (*glycine*), $NH_2CH_2.COOH$, affords a very interesting ampholytic behaviour. It is both an acid and a base and can ionise in two ways, depending on the base or acid added to its solution.

(1) $NH_2CH_2COOH + H_2O \Longleftrightarrow {}^+NH_3.CH_2COOH + OH^-$

(2) $NH_2CH_2COOH + H_2O \Longleftrightarrow NH_2CH_2.COO^- + H_3O^+$
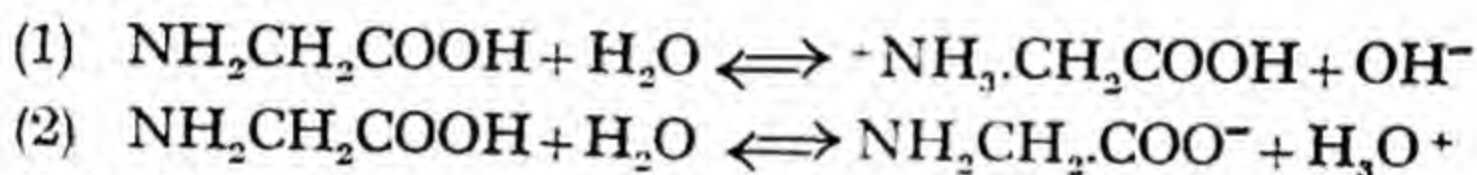
If both types of ionisation occur from the same molecule, an ion carrying both a positive and a negative charge is left. Such ions are called **zwitter** or dual or bipolar ions.

$$NH_2CH_2COOH + H_2O \Longleftrightarrow {}^+NH_3.CH_2.COO^- + H_2O.$$
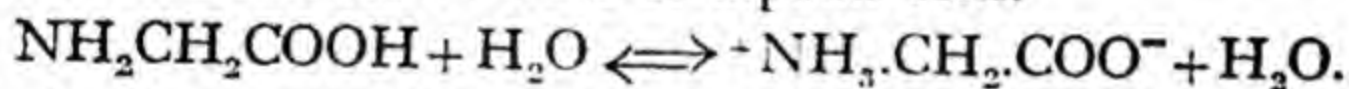
Probably an amino acid exists in aqueous solution almost wholly as *zwitter* ions.

*p*H AND INDICATORS

The H$^+$ ion Concentration (C_H or [H$^+$]) in water Medium —The most important property of acids and bases is that they change the hydrogen ion concentration, C_H *i.e.*, [H$^+$] of water. Acids increase the C_H and bases decrease the same. But, as already pointed out (P. 263), in any aqueous solution *the product of [H$^+$] and [OH$^-$] ion concentrations is always constant at a definite temperature* and is called the ionic product for water (K_w). At room temperature (25°C) the value of this ionic product is 10^{-14}, *i.e.*

$$K_w = [H^+] \times [OH^-] = 10^{-14} \text{ at } 25°C.$$

In pure water, both the ions have the same concentration each equal to 10^{-7}(N); in acid solution [H$^+$] ion concentration predominates while in alkaline solution [OH$^-$] ions are in excess, but the product [H$^+$] and [OH$^-$] has always the same value.

Many chemical phenomena in aqueous media are strongly dependent on the C_H^+ of a solution and so the C_H^+ of a solu-

tion is of great importance to science and industry. The C_H^+ of a solution, however, can be expressed in various ways. For example, in a one-thousandth normal (N/1000) HCl solution, the C_H^+ is N/1000. We can as well express this C_H^+ as 1/1000 gram equivalent per litre *i.e.* $1/10^3$ gm. equivalent per litre *i.e.* 10^{-3} gm. equivalent per litre. The C_H^+ of any solution can thus be expressed as a power of ten and this power of ten of any dilute acid solution (less than normal) is obviously a negative number. So a clever way has been devised to express C_H^+, and this is just to mention this power of ten without the negative sign and call it *p*H. Thus, for the N/1000 HCl solution the C_H^+ is 10^{-3} gm. ion per litre and therefore, the *p*H is 3. So, *p*H is just a compact way of expressing the hydrogen ion concentration of a solution. This notation for expressing C_H^+ was first introduced by Sorensen.

H⁺ Ion Exponent or *p*H—So, we can formally define the *p*H of a solution as the *negative exponent of its hydrogen ion concentration i.e.* logarithm of hydrogen ion concentration with a negative sign. Expressed algebraically,

$$pH = -\log_{10}[H^+] \qquad \cdots \qquad \cdots \quad (1)\text{-XIX}$$

where [H⁺], as usual, stands for hydrogen ion concentration.

The idea is more simply grasped by noting that *a ten-fold decrease in hydrogen ion concentration corresponds to an increase of one pH unit.* In other words, a solution of *p*H 3 has ten times stronger hydrogen ion concentration than one of *p*H 4, and *p*H 4 in its turn implies ten times more C_H^+ than *p*H 5, and so on. It therefore also follows that doubling the hydrogen ion concentration will decrease the *p*H by log 2 *i.e.* by 0·30 units. So if a N/1000 HCl solution has *p*H equal to 3, a N/500 solution will have *p*H equal to 2·70.

_p_H of Acid Solutions—It is thus clear that roughly speaking, a N/1000 solution of a strong acid say, HCl has a *p*H 3, a N/10,000 solution of HCl has a *p*H 4, and so on. If a solution has [H] = ·01N = 10^{-2}(N) its *p*H = 2, if [H⁺] = 10^{-7} [N], then *p*H = 7, and so on.

The question arises what is the *p*H of say, a N/5000 HCl solution. This can be easily done by writing N/5000 as a power of ten. Now C_H^+ = N/5000 = 1/5000 gm. ion per litre = 0·2 × 10^{-3} = $10^{-3·7}$ gm. ion per litre (that 0·2 × 10^{-3} = $10^{-3·7}$ can be easily found out with the help of a log table). Since, C_H^+ = $10^{-3·7}$ gm. equivalent per litre, we easily see that the *p*H = 3·7. Such calculations can be made for any dilute solution of a strong acid and these agree fairly well with experimental values. Weak acids, owing to incomplete dissociation, have much lower C_H^+ and so, much higher *p*H than that obtained by this type of calculation, but once the [H⁺] is known by some means, the *p*H can be calculated in the above way.

pH of Alkaline Solutions —The pH of alkaline solutions can be easily computed if we know the C_{H^+} of such solutions. This can be done with the help of the ionic product equation for water, i.e., $K_w = C_{H^+} \times C_{OH^-}$. For example, a N/1000 caustic soda solution has $C_{OH^-} = 10^{-3}$ gm. equivalent per litre. But since $C_{H^+} \times C_{OH^-} = K_w = 10^{-14}$ at 25°C, we have for this solution $C_{H^+} = K_w/C_{OH^-} = 10^{-14}/10^{-3} = 10^{-11}$ gm. ion per litre and therefore the pH of this solution is 11.

So, all alkaline solutions should have a pH higher than 7 and usually the pH value would lie in the range 7 to 14 at 25°C, and all acid solutions should have a pH lower than 7 and the pH value would usually be in the range 0 to 7 at 25°C. Pure water has a C_{H^+} of 10^{-7} gm. equivalent/litre at 25°C and so its pH is 7 at 25°C. Since K_w changes with temperature, these pH values would also change somewhat with temperature.

An approximate idea of the acidity or alkalinity of a solution can be obtained at a glance from the following table.

Hydrochloric Acid Solution				Pure water			Caustic Soda Solution			
$\frac{N}{10}$	$\frac{N}{100}$	$\frac{N}{1,000}$	$\frac{N}{10,000}$	$\downarrow$			$\frac{N}{10,000}$	$\frac{N}{1,000}$	$\frac{N}{100}$	$\frac{N}{10}$
pH:— 1	2	3	4	5 6 7 8 9			10	11	12	13

For example, $pH = 3$ means an acid solution, having the same acidity as a N/1,000 HCl solution; $pH = 11$ means an alkaline solution having its alkalinity as a N/1,000 NaOH solution; $pH = 2.3$ means an acid strength somewhere between a centinormal and a thousandth normal HCl solution.

EXAMPLE 1. *Calculate the pH of pure water, and also the values of N/1000, N/50 and N/200 solutions of HCl as well as of NaOH at 25°C; Assume complete dissociation of the acid and the alkali.*

In pure water, $[H^+] = 10^{-7}$ (N)   ∴ $pH = -\log [H^+] = -\log 10^{-7} = 7$

In N/1000 HCl, $[H^+] = 10^{-3}$ (N)   ∴ $pH = -\log_{10} 10^{-3} = 3$

In N/50 HCl, $[H^+] = .02$ (N)   ∴ $pH = -\log_{10} (.02) = 1.7$

In N/200 HCl, $[H^+] = .005$ (N) $= pH = -\log .005 = 2.3$

In N/1000 NaOH, $[OH^-] = 10^{-3}$ (N)

   ∴ $[H^+] = K_w/[OH^-] = 10^{-14}/10^{-3} = 10^{-11}$

   ∴ $pH = -\log 10^{-11} = 11$

In N/50 NaOH, $[OH^-] = .02$ (N)

   ∴ $[H^+] = K_w/[OH^-] = 10^{-14}/2 \times 10^{-12}$

   ∴ $pH = -\log [H^+] = -\log (.5 \times 10^{-12}) = 12.3$.

EXAMPLE 2. *Calculate the [H$^+$] ion concentration of three solutions of pH equal to 3.4, 2.1 and 10 respectively.*

Now, $pH = -\log_{10} [H^+]$ or $[H^+] = 10^{-pH}$

   $pH = 3.4$ ∴ $[H^+] = 10^{-3.4} = 0.000398$ (N)

   $pH = 2.1$ ∴ $[H^+] = 10^{-2.1} = 7.94 \times 10^{-3}$ (N)

   $pH = 10.0$ ∴ $[H^+] = 10^{-10}$ (N).

Experimental Determination of *p*H—The common methods of determination of *p*H can be classified into two types

    (1) *E. M. F. methods*

and (2) *Methods using Acid-base Indicators.*

The E. M. F. method using hydrogen electrode serves as the ultimate standard in *p*H determination, though glass electrode, quinhydrone electrode, and many other electrodes are also in use. The indicator method is, however, experimentally the most convenient.

Hydrogen Electrode Method for *p*H Determination—The solution (*x*) (Fig. 97) is taken in a vessel of suitable shape and in it is dipped a *platinised platinum electrode* (platinum foil covered with platinum black by electrolysis). A steady stream of *moist hydrogen* is passed through the solution over the electrode.
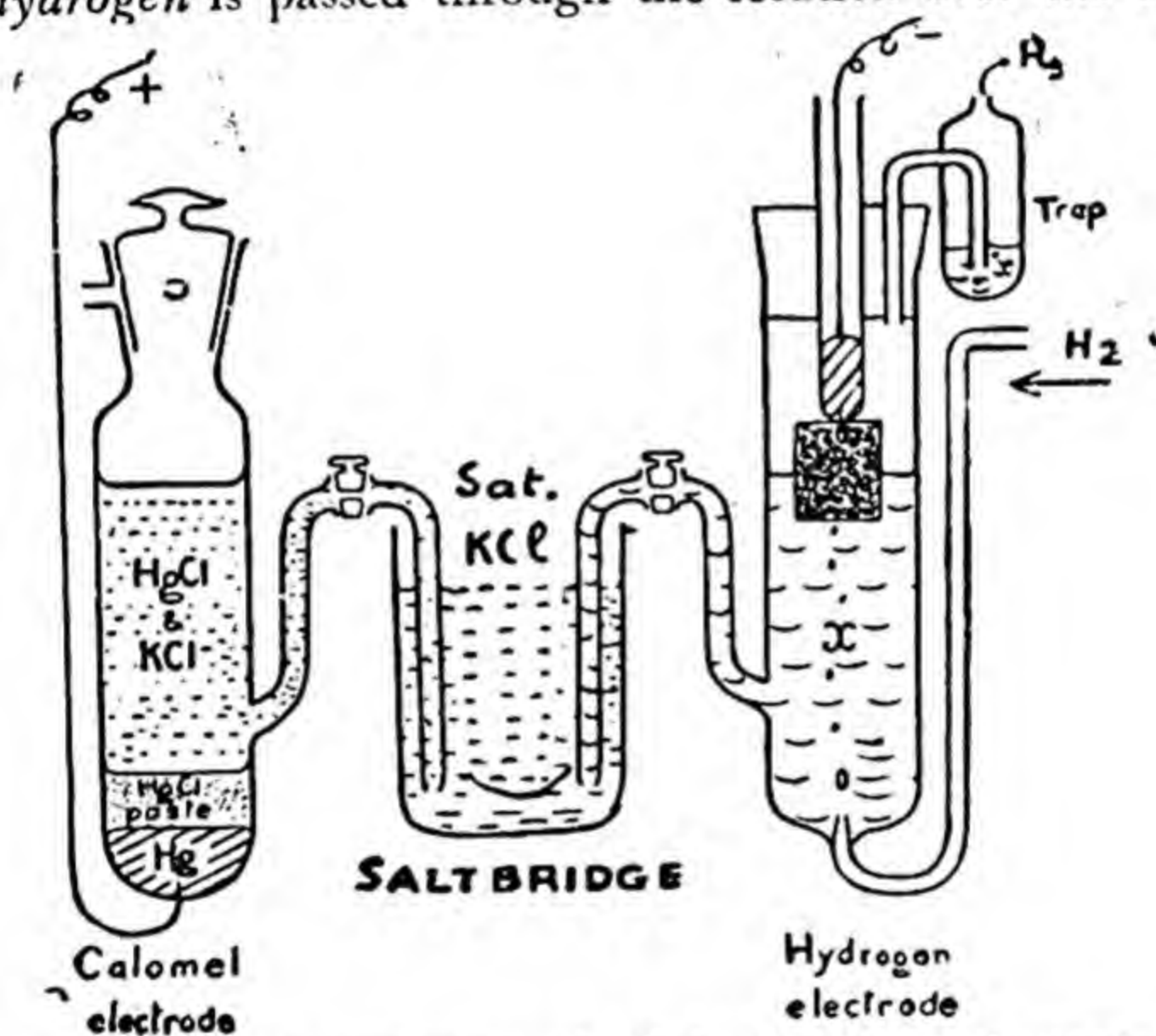
Fig. 97—Determination of *p*H by Hydrogen Electrode

The other half-cell is a *normal calomel electrode* and the two half cells are joined through an intervening saturated solution of potassium chloride (*salt bridge*) to eliminate liquid junction potential. When equilibrium has been attained, the total E.M.F. of the cell (E) is measured by a potentiometer, which substituted in the following equation [eqn. (19), *see* P. 291] gives the *p*H value of the solution.

$$p\mathrm{H} = \frac{E - E \text{ calomel}}{0\cdot059} = \frac{E - 0\cdot281}{0\cdot059} \quad \dots \quad \dots \quad (2)\text{-XIX}$$

Indicator method of *p*H determination—This consists simply in adding a suitable indicator to the solution such that the *p*H of the solution is within the colour change interval of the

indicator and matching the colour, thus produced, against the colour produced by standard buffer solutions under otherwise identical conditions. For rapid measurement a universal indicator which is sensitive over the whole pH range, $i.e.$ from 0 to 14, can be used.

Standard of pH Measurement. Buffer Solution —It is expedient for comparison, preparation and measurement of pH to have in stock solutions of known pH. If such a solution is made by proper dilution of a standard acid or alkali it is found that, due to impurities from the vessel or air, the values of pH of such solutions slowly change, and never attain a steady value. So a solution of standard pH is useful if not only its pH is accurately known, but also it has to some extent, some reserve power of neutralising acid or alkali so as to have a steady pH value.

Such *a solution of known pH which has some reserve power of neutralising acids and bases so that it maintains a steady value of its pH, is called a buffer solution.* Buffer solutions are extensively used in the laboratory as standards in pH measurements.

Buffer solutions usually contain a weak acid or base in company with its salts, $e.g.$ acetic acid and sodium acetate solution, ammonia and ammonium chloride solution, etc. The mechanism of buffer action is comparatively simple. The buffer solution referred to neutralises acid (H^+ ion) according to:— $H^+ + CH_3COO^- \longrightarrow CH_3COOH$ and counteracts alkalies (OH^- ion) as:—$OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$ and therefore tends to maintain a steady pH.

Importance and Usefulness of pH—Fundamentally speaking, the pH of a solution is a very important factor in determining the equilibrium and kinetics of any proton transfer reaction. Thus, the extent of ionisation of weak acids depends on the pH of a solution, and many chemical reactions in solution is sensitive to the acidity or alkalinity of the solution. Its technological usefulness is manifold. In drugs, fermentation, bakery, confectionery, emulsification, froth floatation, scouring, sizing, fountain pen inks, and many others, a strict control of pH is obligatory. In biological science the importance of pH can not be overemphasised as most living matter maintains by internal buffering a constant pH in its various regions; for example, human blood has a pH of 7.4 and injectules are to be made to equilibriate easily with this pH.

ACID-BASE INDICATORS

Indicators—Indicators are substances which are used to indicate, generally by their colour change, specific physico-chemical condition of chemical systems. Thus, we have the ordinary *acid-base indicators* like litmus, etc. used for acidimetric titrations. Another class is constituted by the *oxidation-reduction indicators* to denote the degree of oxidation of a solution; diphenylamine is a familiar example of this class

and is used to indicate the end point of the oxidation of ferrous ion by dichromate by a deep blue colour. A third class of indicators is the *adsorption indicators*, a good example being the red dye eosin. If a solution of a chloride is titrated with silver nitrate solution in presence of this red dye, the white precipitate of silver chloride suddenly becomes red at the end point due to adsorption of this dye. There are many other types of indicators too, such as starch paste as iodine indicator, radioactive indicators, metalochromic indicators, etc. In the following discussion we shall however limit ourselves to a study of *the neutralisation indicators* only.

Theory of Indicators: Chemical Nature —From physico-chemical point of view, indicators may be regarded as very weak organic acids, capable of dissociation like all acids into hydrogen ion and an anion as represented by $HIn \Longleftrightarrow H^+ + In^-$. The main and common characteristic of all indicators is that the colour of a solution containing an indicator will depend on the relative proportion of the unionised molecule HIn and the anion In^-.

Mechanism of Colour Change—To clearly represent that In^- has a colour different from the HIn, we should represent it as In^{*-} and so the dissociation process is represented—

$$HIn \Longleftrightarrow H^+ + In^{*-} \qquad \dots \qquad \dots \quad (3)\text{-XIX}$$
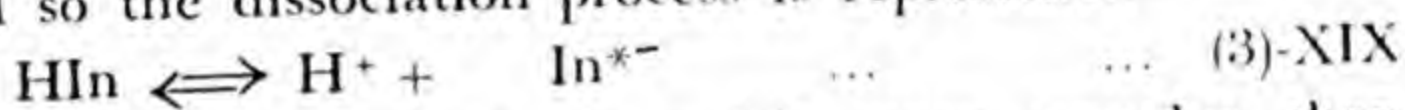
The actual state of affairs is a bit more complex than described above. The indicator acid, HIn first undergoes a reversible tautomeric change into a substance of different colour, HIn^* which is capable of ionisation, the whole equilibrium being represented—
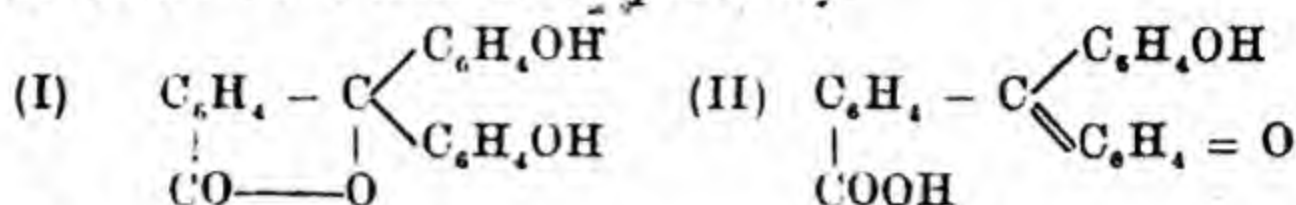
$$HIn \Longleftrightarrow HIn^* \Longleftrightarrow H^+ + In^{*-}$$

But in order that a substance may be a good indicator the concentration of HIn^* is usually very small and so the simple dissociation equation (3) is sufficient for our purpose and is therefore generally used.

If a few drops of an acid are added to an indicator solution, the acid, by virtue of the large concentration of H ions it produces by dissociation, checks the above ionisation of the indicator acid. The solution would then contain a large excess of HIn molecules, whose colour will, therefore, be the *'acid colour'* of the solution. If a small excess of alkali, say, NaOH is added to the solution, sodium salt of the indicator will be formed which being a salt will ionise almost completely giving a great excess of In^{*-} ions, whose colour will be the *'alkaline colour'* of the indicator. For a bi-colour indicator, if the solution contains an equal concentration of HIn molecules and In^{*-} ions, the solution shows the *'neutral colour'* of the indicator.

Structural Relation between the two Forms—The real cause for such difference in colour between the anion and the unionised molecule has been found to be a *tautomeric transformation* of the HIn molecule to another modification called the *quinonoid*

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form which has a different colour and ionises almost completely to form In*⁻. In the case of phenolphthalein, for example, the ordinary form (colourless) and quinonoid form (pink colour) are represented below as I and II respectively.

$$(I) \quad C_6H_4 - C\begin{cases} C_6H_4OH \\ | \quad C_6H_4OH \\ CO\text{——}O \end{cases} \qquad (II) \quad C_6H_4 - C\begin{cases} C_6H_4OH \\ | \\ COOH \end{cases} C_6H_4 = O$$

Useful Indicators —That a substance responds to a change of hydrogen ion concentration with a change of colour is not a sufficient condition for it to be used as an indicator. The characteristics of a good indicator are—

(*a*) The change of colour should be *sharp, i.e.* the change of colour should occur over a short range of hydrogen ion concentration.

(*b*) The colour should be *stable* and brilliant, and the colour change should be between *contrasting colours.*

(*c*) The colour change should be at the *end point of the reaction* being studied.

A considerable number of indicators have been so far brought to light, but owing to the above considerations only a few have found place in the laboratory.

Indicator Equilibrium —Since indicators are weak electrolytes they would obey Ostwald's dilution law; their equilibrium may be represented as—

$$\frac{[H^+][In^{*-}]}{[HIn]} = K_{in} \qquad \text{or, } [H^+] = K_{in}\frac{[HIn]}{[In^{*-}]}$$

where K_{in} is the *dissociation constant* of the indicator. When an indicator shows the '*neutral colour*' we must have [HIn]= [In*⁻], since HIn and In*⁻ are respectively responsible for the acid colour and the alkaline colour of the indicator.

∴ *for neutrality,* $[H^+] = K_{in}.$

Since the indicator constants. K_{in} for different indicators are different, we arrive at the very important result that *the concentration of hydrogen ion at which an indicator indicates neutrality is constant for the same indicator and is different for different indicators.* The following two experiments are illustrative of this point.

EXPERIMENT 1. Take a roughly decinormal solution of sodium carbonate, and add a few drops of phenolphthalein and drop by drop a dilute HCl solution, until the pink colour of phenolphthalein is just discharged. Test this solution—which is now distinctly acidic to phenolphthalein—with a few drops of methyl orange indicator. The methyl orange turns yellow showing that the solution is alkaline to methyl orange.

EXPERIMENT 2. To a solution of methyl orange add a few drops of a very dilute HCl solution, to make the colour just red (acidic). Dilute the solution with freshly prepared distilled water only. The colour of the solution slowly changes from red to yellow (alkaline colour).

Sensitivity Range of Indicators, etc. —It is thus theoretically and experimentally established from the foregoing equations

and experiments that *different indicators indicate neutrality at different H+ ion concentrations or pH.* In fact, the colour of an indicator changes over a certain *p*H range, sometimes called 'colour change interval' or 'sensitivity range' and within this colour change interval there is a definite *p*H for each indicator at which it shows its *'neutral colour'.* From the following table of indicators, giving their range of colour change, neutral colour *p*H, etc. it will be observed that the *p*H at which an indicator exhibits 'neutral colour' varies widely with different indicators; phenolphthalein shows 'neutral colour' in the alkaline region (*p*H=8·5), litmus exhibits the same with a neutral solution (*p*H=7) while methyl orange points to neutrality in a distinctly acid region (*p*H=4).

Indicator	*p*H range of colour change	Acid—Alkaline colour colour	Neutral colour *p*H
Methyl Orange	3·1—4·4	*Red—Orange yellow*	4·0
Methyl Red	4·2—6·3	*Red—Yellow*	5·0
Litmus	5·0—8·0	*Red—Blue*	7·0
Phenolphthalein	8·2—10·0	*Colourless—Pink*	8·5
Thymolphthalein	9·3—10·5	*Colourless—Blue*	10·0

Suitability of Indicators in Titrations—This can be well understood with the help of *p*H—titration curves (Fig. 98). The *p*H change during titrations of strong acids and weak acids by a strong base is shown in Fig. 98. The most interesting part of this figure is that near the equivalence point there is a jump in *p*H. So, an indicator whose neutral colour *p*H lies within this range is suitable for our purpose.

Evidently, almost any indicator would be suitable for titration of a strong acid by a strong base, because this jump in *p*H is over a wide range from *p*H 3 to 9. The jump is, however, much less for weak acids and lies in the alkaline region (for acetic acid from about 5·5 to 9).

Fig. 98—*p*H change during Titration of acids by an alkali

To titrate a weak acid with a strong base, *e.g.* acetic acid with caustic soda, we have therefore, to use an indicator showing its neutral colour in the alkaline region, viz. phenolphthalein (*p*H =8·5). To tritrate a strong acid with a strong base most indicators are suitable since one drop of excess of the acid will bring about

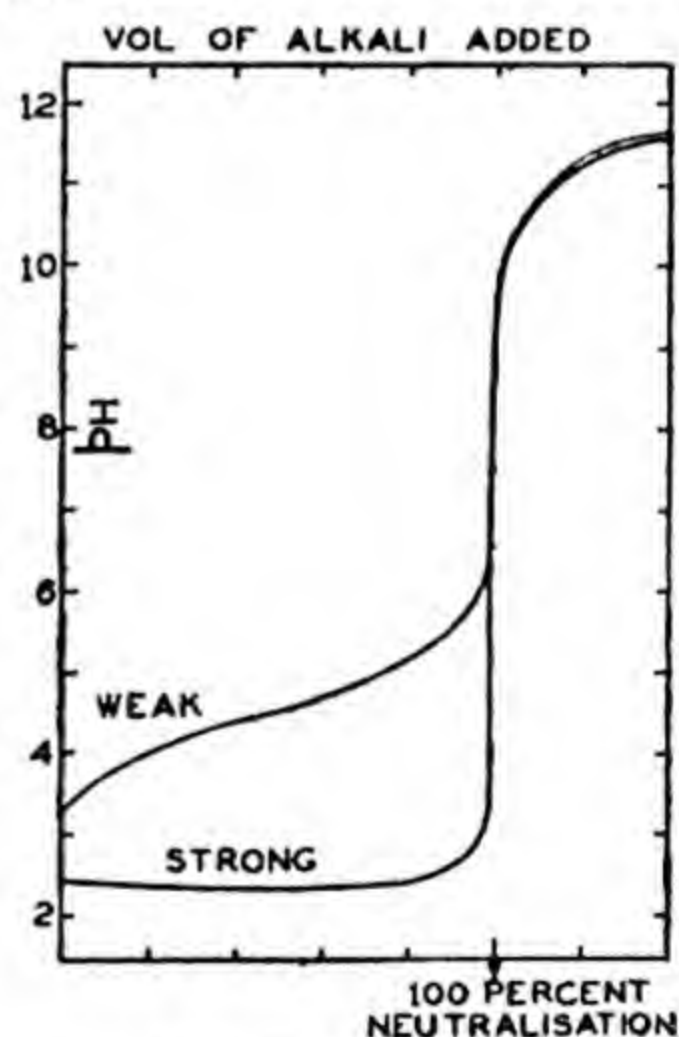an enormous change in hydrogen ion concentration of the solution. To titrate a weak acid with a weak base, no indicator is suitable since such a solution on addition of alkali or acid during titration changes its pH very slowly like buffer solutions. The results are appended below.

From a similar type of reasoning, in order to titrate weak base with a strong acid, e.g. ammonia with hydrochloric acid, where the solution will be acidic at the *equivalence point*, the indicator used would be of such a character as to show its 'neutral colour' in an acid region; such an indicator is methyl orange, which indicates neutrality at $pH=4$.

Titrations	Suitable Indicator	pH of colour changes
Strong acid and *strong* base	Any	$pH=5$ to 9
Strong acid and *weak* base	Methyl Orange	$pH=4$
Weak acid and *strong* base	Phenolphthalein	$pH=8.5$
Weak acid and *weak* base	None satisfactory	slow change of pH

Explanation of the Inflexion in the Titration Curve —Suppose we add N/10 alkali in steps of 0.1 c.c. to 10 c.c. N/10 acid. Now the percentage of acid neutralised for each addition of alkali determines the corresponding pH change. Evidently at the beginning 0.1 c.c. neutralises only 1% of the acid but near to the equivalence point, say after 99% neutralisation, the same 0.1 c.c. causes 100% change of the acid in the solution, and so at the equivalence point the percentage change of acidity for a given value of alkali added is highest. Therefore, the pH neutralisation curve is the steepest at the equivalence point. This is the principle on which all titrations are based.

Exercise

1. Write short notes on (a) pH value of solution (b) Buffer solution (c) Indicators.

2. Calculate the pH of the following solutions :—(a) 1 gm. of NaOH dissolved in 400 c.c.; (b) 1 gram of HCl dissolved in 800 c.c. of water; (c) a mixture of solutions (a) and (b); (c) 100 c.c. of water containing 3 drops (.05 c.c.) of N HCl; (d) a N/25 NaOH solution.

[12.8; 1.46; 3.7; 3.82 12.6]

3. What is in an indicator ? What determines its sensitiveness ? What indicator would you use in titrating acetic acid with caustic potash ? Give reasons for your answer.

4. Why is methyl orange called an indicator ? What does it indicate ? How would you define an acid aqueous solution ? Explain why methyl orange is used in the titration of total alkalinity and phenolphthalein is used for the estimation of alkali carbonates in the presence of bicarbonates.

5. What is an indicator? What indicator would you use (a) in titrating sulphuric acid with sodium carbonate, and (b) in titrating acetic acid with caustic potash ? Give reasons for your answer.

6. Calculate the pH of decinormal solutions of nitrous acid and nitric acid respectively (K$_c$ 0.45×10^{-3})　　　　[2.17; 1]

(Hint :—Calculate a from dilution law; now, $H^+ = a\,c$ and from H^+ calculate pH).

PART IV

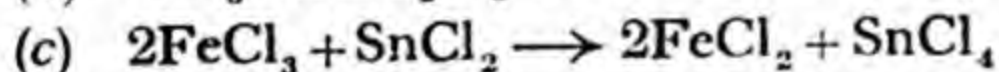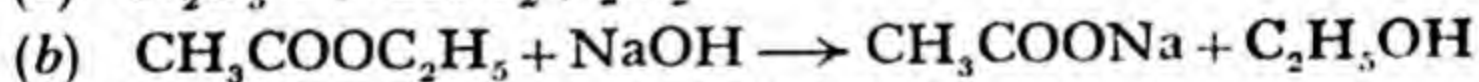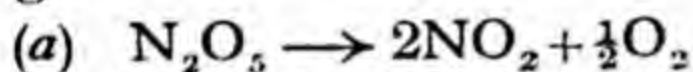# PASSAGE TOWARDS EQUILIBRIUM

Speed of Reactions—Catalysis.

SPEED OF REACTIONS

Introduction —We were engaged in a previous section (Part II) in studying chemical equilibria *i.e.* how far a chemical reaction would go, but omitted to refer to how fast that equilibrium would be attained. This will be the subject of the present chapter.

All chemical reactions take some time for completion and we are familiar with chemical reactions of all speeds ranging from extremely fast to extremely slow ones. Reactions between ions in solution which do not involve a change in oxidation state are generally very fast, for example, acid-base neutralisation, precipitation of say, barium sulphate by double decomposition, etc. On the other hand, ionic oxidation-reduction reactions are very often quite slow, because they involve actual transfer of electrons, and many examples of slow reactions are already familiar to the student during oxidation-reduction titrations, *for example*, the slow discharge of colour of permanganate in acid solution by hydrogen peroxide, slow precipitation of mercurous chloride by reduction of $HgCl_2$ by $SnCl_2$, etc. Heterogeneous reactions are slow by their very nature, a well-known example being weathering of rocks. Organic reactions as a class generally proceed slowly, a fact which is apparent from the heating often under reflux for long periods necessary during organic preparations.

Classification and Nomenclature—For purposes of kinetics the reactions are classified according to the number of molecules reacting—

    (*a*) $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

    (*b*) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

   (*c*) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

Thus, the decomposition of nitrogen pentoxide [reaction (*a*)] is called a *mono-molecular* or *first-order* reaction, since only one molecule decomposes to form a number of products. Similarly, reaction (*b*) representing the hydrolysis of ester by alkali is a *bi-molecular* or *second-order* reaction, and reaction (*c*) is a *ter-molecular* or *third-order* reaction.

It might be argued that we could as well write reaction (*a*) as $2N_2O_5 \longrightarrow 4NO_2 + O_2$ and class it as a second-order reaction. This is not permissible as the observed reaction speed is directly proportional to the concentration of the pentoxide. If the observation was otherwise, say, if the observed speed was proportional to the square of the concentration of the pentoxide, it would have been classed as a bi-molecular reaction in the above manner. However, a similar reaction, the decomposition of hydriodic acid is experimentally found to have a reaction speed proportional to the square of its concentration and so is classed as a bi-molecular reaction and written as $2HI \longrightarrow H_2 + I_2$ and not $HI \longrightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$. Thus, rate determination provides an insight into chemical reactions.

Hence, we may remark that chemical equations totally fail to supply information about the order of a particular reaction, for which we have to turn to a determination of reaction speed; in fact, it is very common to meet with reactions involving three or more molecules classed as second order ones. For this reason, all modern authors have discontinued the use of the terms, mono-molecular, bi-molecular, etc., and prefer to use first-order, second-order, etc. in their places.

Hence, a first order reaction is defined as one in which the absolute rate of change is proportional to the first power of the concentration of the reacting substance and not as one in which only one molecule decomposes. Similar remarks also apply to second and third-order reactions.

Mathematical Formulation of First-order Reaction—If one molecule decomposes chemically to form a number of other substances, the reaction speed according to the law of mass action is, at any instant, proportional to the concentration of the substance at that instant. Taking for example, the first-order reaction, the decomposition of N_2O_5 gas, according to the equation,

$$N_2O_5 \longrightarrow 2NO_2 + \tfrac{1}{2}O_2$$
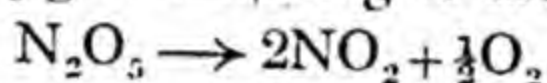
if we start with 'a' mols of the pentoxide and if 'x' mols are decomposed in time t secs, then $(a\text{-}x)$ is proportional to the concentration of the pentoxide at that instant. The speed of the reaction i.e., the rate at which the concentration of the pentoxide decreases with time, t, is according to the mass-law proportional to the concentration of the pentoxide, $(a\text{-}x)$. Expressed mathematically,

$$-\frac{d[N_2O_5]}{dt} \propto [N_2O_5]$$

or, $-\dfrac{d(a-x)}{dt} \propto (a-x)$ or $\dfrac{d(a-x)}{dt} = -k_1(a-x)$

where k_1 is the proportionality constant to be called first-order *velocity constant* or *specific reaction rate*.

[Note the minus sign in the first equation, which signifies the decrease of the pentoxide concentration with time.]

This equation is a differential one i.e. involves infinitesimally small quantities and is to be integrated before this can be applied to experimental results.

Integrating, we get,

$$\int \frac{d(a-x)}{(a-x)} = -k_1 \int dt$$

or $ln\,(a-x) = -k_1 t + \text{constant}$.   (*ln* means $\log_e$)

The value of the constant may be evaluated by substituting $x=o$ and $t=o$ in the above equation in conformity with the known fact that at the beginning (i.e. $t=o$) there is no decomposition (i.e. $x=o$). The equation then becomes,

$$ln\,a = \text{constant}$$

Substituting this value of the constant, we get

$$ln\ (a-x) = -k_1 t + ln\ a$$

or, $$ln\ \frac{a}{a-x} = k_1 t$$

This equation is in natural logarithm and to convert it into ordinary logarithm, we have no multiply it by 2·303, and so the final equation becomes,

$$\frac{2\cdot303}{t}\ log_{10}\ \frac{a}{a-x} = k_1 \qquad \ldots \qquad \ldots \qquad (1)\text{-XX}$$

giving the velocity constant or the specific reaction rate of a first-order reaction, k_1 in terms of measurable quantities, viz. the fraction decomposed in a given time.

If we put $a-x=c$ i.e. concentration, we get

$$log\ c = -\frac{k_1}{2\cdot303} t + log\ a \qquad \ldots \qquad \ldots \qquad (1a)\text{-XX}$$

i.e. log c plotted against t gives a straight line of negative slope. This is shown in Fig. 100 for N_2O_5 decomposition.

Time of Half-Decomposition —The time required for half decomposition, T is easily obtained by putting $x=a/2$ in equation (1), when we get,

$$T_{\frac{1}{2}} = \frac{2\cdot303\ log\ 2}{k_1} = \frac{0\cdot693}{k_1} = \text{constant} \qquad \ldots \qquad (2)\text{-XX}$$

i.e. in a mono-molecular reaction the time of half-decomposition or period of half change is a constant. The significance of this statement is that if half of the substance decomposes in, say, one day it will be reduced to $\frac{1}{2} \times \frac{1}{2}$ i.e. one fourth in two days, one-eighth in three days and so on. For a mono-molecular reaction this is not only true for half-decomposition but, as can be easily proved, for decomposition to any given fraction and so we may state that *in a first-order reaction the fraction decomposed in a given time is independent of the initial concentration.*

Unit of k_1 —Another interesting point about unimolecular reaction is that the value of the constant k_1 is independent of the unit in which concentration is expressed, since equation (1) involves only ratio of concentrations. However, the numerical value of k_1 depends on the unit in which time is expressed. If time is expressed in seconds, k_1 is in reciprocal seconds (sec^{-1}). It is to be noted carefully that though the value of k_1 in minutes is sixty times its value in seconds, the amount decomposed in one minute is much less than sixty times the amount decomposed in the first one second.

Physical Significance of k_1 —The significance of k_1 needs clear appreciation. Taking a specific case (see next section), viz., the decomposition of H_2O_2, k_1 is 0·0437 min.$^{-1}$. This means that if we have any solution of H_2O_2, 4·37 per cent (or 0·0437 fraction) of H_2O_2 would decompose per minute provided by some means

(say, by adding fresh H_2O_2 from outside) the initial concentration is maintained constant throughout this one minute interval. Note that solutions of H_2O_2 of *any concentration whatsoever* will suffer the same percentage loss per minute. Also, if the imposed stipulation of constant concentration is not adhered to, it can be easily shown from equation (1) that the per cent decomposed per minute will be somewhat less, *viz.*, 4·26 per cent per minute. So, the physical significance of k_1 is the *fraction decomposed in unit time at constant concentration.*

Examples of First Order Reaction—(a) Gaseous Reactions— Examples of first order reaction in the gaseous phase are not many. The classical example is the decomposition of nitrogen pentoxide which has been intensively investigated and has been found to obey closely the first order equation not only in the gaseous phase but also in solution ;

$$N_2O_5 \longrightarrow N_2O_4 + \tfrac{1}{2}O_2$$
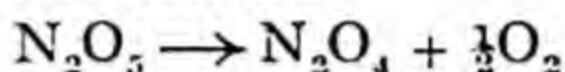
Some other examples of homogeneous gaseous first order reaction not too complicated by side effects, are the decomposition by heat (called pyrolysis) of acetone, azomethane and dimethyl ether.
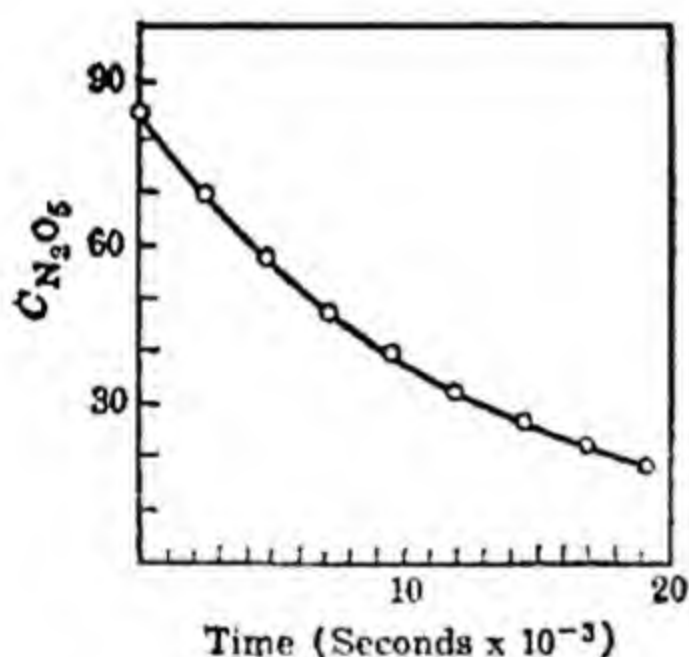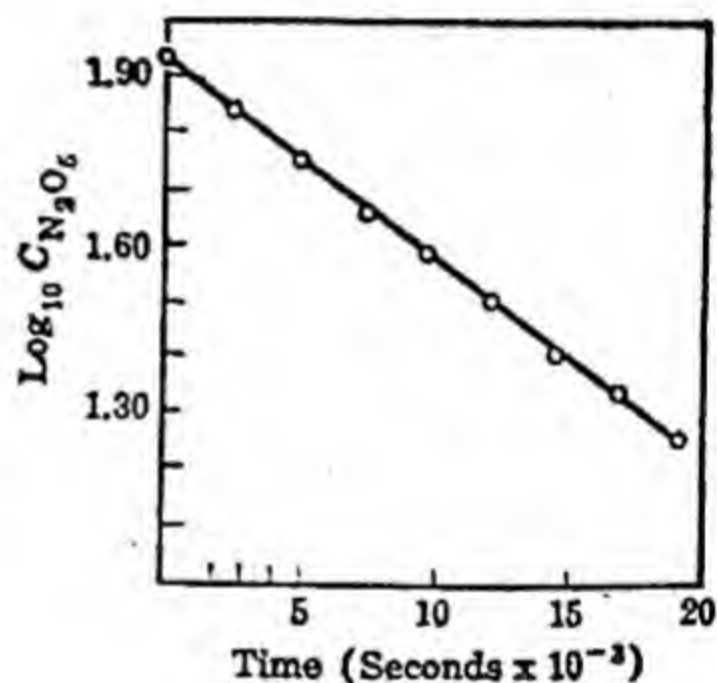

Fig. 99—$C_{N_2O_5}$ versus time

Fig. 100—Linearity of log $C_{N_2O_5}$ versus time

Fig. 99 graphically represents the decomposition of N_2O_5 showing the decrease of concentration of N_2O_5 with time. The same data have been plotted as log c against time in Fig. 100 wherein it would be seen that a good straight line is obtained in agreement with equation (1a) proving this to be a first order reaction.

There are a number of other reactions which though following a first order equation have been found to take place partly or entirely on the surface of the reaction vessel or a catalyst. Thus the decompositions of the phosphine, PH_3 or arsine, AsH_3 are first order gaseous reactions, taking place almost entirely on the surface *i.e.* wall of the container. Such reactions are often called *wall-reactions*. Similarly, N_2O decomposes catalytically by a first order equation almost entirely on the surface of a hot gold wire introduced in the vessel.

Another type of reaction which takes place entirely on the wall or at least requires a third body is the recombination of atoms to molecules (for example, $H + H = H_2$, $N + N = N_2$, etc.) because if there is no third body to drain out the high exothermic energy of these reactions, the molecules can hardly contain so much energy and again fall apart into atoms. The atomic hydrogen torch or the glow of 'active' nitrogen is due to the above type of recombination reaction on a solid surface.

(b) First order Reactions in Solution—We have already mentioned that N_2O_5 decomposition is of first order not only in the gaseous phase but also in solution. However, the most extensively investigated is the decomposition of hydrogen peroxide in solution which is catalysed by various substances, viz., by finely divided metals, such as platinum, gold, etc., by the enzyme called blood catalase, and by the iodide ion.

The reaction can be easily followed by keeping a solution of the peroxide (about 0·2N) at constant temperature in contact with the catalyst. Ten c. c. portions of the solution are withdrawn after definite intervals of time and are quickly run into 100 c. c.

HYDROGEN PEROXIDE DECOMPOSITION

Time, (minutes)	Permanganate Titre. $(a-x)$	H_2O_2 decomposed in c.c. $KMnO_4$, x	Specific Reaction Rate, k, per minute
0	46·1	0	....
5	37·1	9·0	0·0435
10	29·8	16·3	0·0438
20	19·6	26·5	0·0429
30	12·3	33·8	0·0440
50	5·0	41·1	0·0444
			Mean 0·0437

iced water to check further progress of the reaction. The concentration of the peroxide is determined by titration with a standard permanganate solution. The foregoing table is compiled on the basis of such an experiment at 20°C. Since in unimolecular reaction it does not matter in which units the concentrations are expressed, we have adopted here the volume of permanganate as a measure of the concentration of the peroxide. It would be observed that the calculated velocity constants according to equation (1) remain sensibly constant throughout the course of the reaction.

Another very illustrative case of unimolecular reaction in solution is the conversion of hydroxy-valeric acid to valerolactone according to the equation:—$C_4H_8(OH)COOH \longrightarrow C_4H_8OCOO + H_2O$ in presence of dilute acid as catalyst. As the reaction proceeds, hydroxy-valeric acid disappears and so, the reaction is easily followed by titrating a measured volume of the reaction mixture

with standard base from time to time. The following table gives the volume of alkali required to titrate the acid after definite intervals of time and the calculated specific reaction rates, k_1 according to equation (1), remain admirably constant in both the experiments.

CONVERSION OF HYDROXY-VALERIC ACID INTO VALERO-LACTONE BY 0·25 (N) HYDROCHLORIC ACID AT 25°C

Time, mi	c.c. alkali	$k_1 \times 10^4$	Time, mi	c.c. alkali	$10^4 k_1$
0	19·04	...	0	18·55	...
48	17·60	32·5	46	17·11	39·3
76	16·90	39·0	125	15·18	39·3
124	15·80	39·5	174	14·22	39·5
204	14·41	39·8	221	13·49	39·5
238	13·94	39·3	262	12·97	39·3
289	13·37	39·4	307	12·45	39·5
complete	10·71	...	complete	9·87	...

In addition to the already mentioned classical case of the decomposition of nitrogen pentoxide vapour, many cases of gaseous unimolecular reactions have recently been brought to light. The decompositions by heat (called *pyrolysis*) of the vapours of a number of organic compounds like acetone, aldehydes, etc., are mostly unimolecular and they have been recently studied in great details.

Some More First-order Reactions–The hydrolysis of cane-sugar in presence of dilute acids as catalyst to form glucose and fructose according to the equation—

$$C_{12}H_{22}O_{11} - H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$
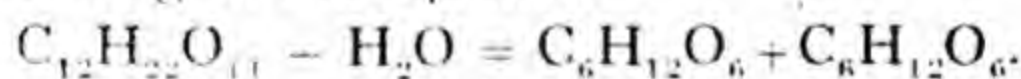
though apparently bi-molecular follows the unimolecular equation. This is because in the above reaction which is usually conducted in aqueous solution, the concentration of water remains practically constant, and so, the reaction speed is proportional only to the concentration of cane sugar. Such reactions are sometimes very inadvertently styled *pseudo-unimolecular reaction* in place of the more appropriate term first-order reaction.

This reaction, called '*inversion of cane sugar*,' since the optical rotation changes from dextro to laevo during the course of the reaction, occupies a prominent position in reaction kinetics as being the first chemical change to be timed in 1850 by Wilhelmy. The reaction is usually followed by observing the optical rotation in a polarimeter. If α_1 is the initial rotation and α_0, the rotation after completion of the reaction and α, the optical rotation at any time, t, then, "a" the total quantity of sugar originally present is proportional to the total change in rotation, $\alpha_1 - \alpha_0$, and $(a-x)$ the fraction of sugar remaining at time, t becomes proportional to the actual change of rotation after this interval i.e. $\alpha - \alpha_0$. These

values when substituted in the first-order equation $kt = \log [a/(a-x)]$, give,

$$k_1 = \frac{1}{t} \ \log \ \frac{x_1 - x_0}{x - x_0} \qquad \ldots \qquad \ldots \text{(3)-XX}$$

Some values of k_1 calculated according to the above equation are given in the following table, showing the hydrolysis of cane sugar (0·44 molal) in presence of 2·5 molal formic acid. The constant, k_1 thus calculated remains fairly constant.

HYDROLYSIS OF CANE SUGAR

Time t (hours)	Observed, Rotation α	$k_1 = \frac{1}{t} \log \frac{a_1 - a_0}{a - a_0}$	Time, t (hours)	Observed Rotation	Velocity constant, k_1
0	57·90 (a_1)		15	28·90	0·0146
2	53·15	0·0146	35	6·75	0·0148
4	48·50	0·0149	52	—2·05	0·0148
6	44·40	0·0147	85	—11·25	0·0146
8	40·50	0·0147	complete	—15·45 (a_0)	
			mean →		0·0147

Another reaction of this type where a truly bi-molecular reaction becomes of first order owing to one of the reactants being the solvent itself is the interaction between acetic anhydride and ethyl alcohol in alcoholic medium according to the equation $(CH_3CO)_2O + 2C_2H_5OH = 2CH_3COOC_2H_5 + H_2O$. This reaction has been studied experimentally and the speed has been found to follow the first order equation.

Mathematical Formulation of Second-order Reaction —Reactions in which two molecules (which may be same or different) take part and the rate is proportional to the concentration of each of them, are called bi-molecular or second-order reactions.

Let the reaction be represented as

$$A + B \longrightarrow C + D$$

If the original concentrations of A and B are a and b respectively and if x represent the number of mols of A or of B decomposed in time, t, then

$$-\frac{dx}{dt} = k_2(a-x)(b-x)$$

where k_2 is second-order specific reaction rate. This equation on integrating by the method of fractional parts yields the equation

$$k_2 = \frac{1}{t(a-b)} \ \log \ \frac{b(a-x)}{a(b-x)} \qquad \ldots \qquad \ldots \text{(4)-XX}$$

If the original concentrations of A and B are equal we have $a = b$ and so,

$$\frac{dx}{dt} = k_2(a-x)^2,$$

which on integration yields

$$k_2 = \frac{1}{t} \frac{x}{a(a-x)} \qquad \cdots \qquad \cdots \quad (5)\text{-XX}$$

It may be noted that since $a - x = c$, the concentration of the substance decomposing, this equation can be put in its reciprocal form, i.e.

$$\frac{1}{c} = k_2 t + \frac{1}{a} \qquad \cdots \qquad \cdots \quad (6)\text{-XX}$$

Half-Decomposition Period—It can be easily seen by putting $x = a/2$ in equation (5) that $T_{\frac{1}{2}} = 1/ak_2$, i.e. the half decomposition period in a second order reaction is inversely proportional to the initial concentration. Thus, we see that both the unit of k_2 and expression for the half decomposition period in second-order reaction are different from that of a first-order reaction.

Experimental Study of Second-order Reactions—Data illustrating this equation are shown in the following table for the hydrolysis of methyl and ethyl acetate by caustic soda solution at 25°C. The reactions are easily followed by withdrawing from the reaction mixture 5 c.c. samples at frequent intervals and titrating the amount of acid present in it with standard alkali after quenching the progress of reaction in the withdrawn sample with excess of iced hydrochloric acid solution.

Ethyl Acetate			Methyl Acetate		
Time, t minutes	Fraction Saponified	$k = \dfrac{x}{t(1-x)}$	Time, t minutes	Fraction Saponified	$k_2 = \dfrac{x}{t(1-x)}$
5	0·245	0·0649	3	0·260	0·117
7	0·313	0·0651	5	0·366	0·115
9	0·367	0·0645	7	0·450	0·117
15	0·496	0·0650	10	0·536	0·115
20	0·566	0·0652	15	0·637	0·117
25	0·615	0·0642	21	0·712	0·118

The reaction can also be followed by measuring the conductivity of the system which will continuously decrease as the fast moving hydroxyl ions are being replaced by the slower acetate ions during the reaction. From the table it will be found that k_2 remains fairly constant during the course of the reaction.

The hydrolysis of ester is brought about by the hydroxyl ions (eqn (a) below) and not by the alkali molecule as represented in the foregoing equation. This is proved by the fact that the reaction speed is bi-molecular even when baryta is used as alkali and not ter-molecular as shown in equation (b).

(a) $CH_3COOC_2H_5 + OH' = CH_3COO' + C_2H_5OH$

(b) $2CH_3COOC_2H_5 + Ba(OH)_2 = (CH_3COO)_2Ba + 2C_2H_5OH$
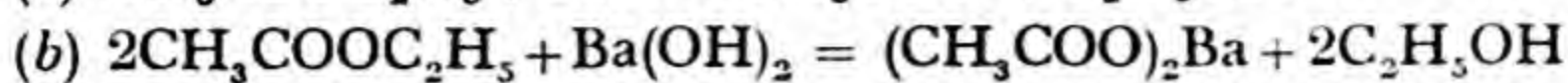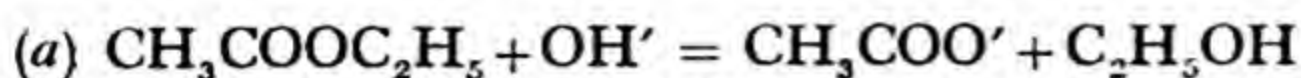
Another good example of a second-order reaction is the conversion of ammonium cyanate into urea according to the equation, $NH_4^+ + CNO^- = CO(NH_2)_2$. This reaction is one of the very few ionic reactions not involving oxidation-reduction which proceed at a measurable speed.

Comparison of First and Second-order Reactions —We summarise below the main features of first order and second order reactions.

	First Order Reaction	*Second Order Reaction*
Specific Rate constants, k_1 and k_2	$k_1 = \dfrac{l}{t} \ln \dfrac{a}{a-x}$	$k_2 = \dfrac{l}{t} \dfrac{x}{a(a-x)}$
Variation of concentration, c with time	log c decreases linearly with t	$\dfrac{1}{c}$ increases linearly with t
Dimensions of k_1 and k_2	Independent of concentration ($time^{-1}$)	Depends of concentration ($time^{-1} Conc.^{-1}$)
Half-decomposition period, $t_{\frac{1}{2}}$	Independent of initial concentration	Inversely proportional to initial concentration.

That the half-decomposition period varies as above is illustrated from experimental data in the following table for the unimolecular decomposition of phosphine ($PH_3 \longrightarrow P + \frac{3}{2}H_2$) and the second order decomposition of N_2O ($2N_2O \longrightarrow 2N_2 + O_2$), where it will be found that the time for half decomposition is constant for the unimolecular reaction but is inversely proportional for the bimolecular reaction.

HALF-DECOMPOSITION PERIOD

Decomposition of Nitrous oxide		*Decomposition of Phosphine*	
Initial Pressure	Half-Life Period (sec.)	Initial Pressure	Half-Life Period (sec.)
296	255	707	84
139	470	79	84
52·5	860	37·5	83

Third-order Reaction—The equation for a third order reaction in which three different types of molecules take part is

$$-\frac{dx}{dt} = k_3(a-x)(b-x)(c-x)$$

where a, b and c are the initial concentrations of the reactants and x denotes the number of mols of each which is decomposed in time t. A special case arises when the initial concentrations are equal *i.e.* $a = b = c$. The equation then becomes

$$-\frac{dx}{dt} = k_3(a-x)^3$$

which on integration changes to

$$k_3 = \frac{1}{t} \cdot \frac{1}{2} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\} \qquad \dots \qquad \dots \quad (7)\text{-XX}$$

The reaction between stannous chloride and ferric chloride in solution according to the equation,

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

has been found by Noyes to be termolecular conforming to the above kinetic equation.

Only a few third order reactions in the gaseous phase are known and they all involve nitric oxide. NO, *viz.* its reaction with Cl_2. Br_2, O_2 or H_2. A remarkable fact about the velocity of the reaction $2NO + O_2 \longrightarrow 2NO_2$ is that *the speed of this reaction decreases with rise of temperature*, though generally, the speed increases two to three-fold per ten degree rise of temperature.

It may however be generally remarked that reactions of an order three or higher do seldom occur and in fact, the termolecularity of the foregoing reactions is on very good grounds doubted by many chemists. The reason for this is that the chance of three or more molecules colliding simultaneously is so remote that the possibility of their occurrence is negligible. The present belief is that a reaction, however complex, is the net effect of a number of simple bi-molecular and unimolecular reactions of varying speeds.

Zero-order and Fractional order Reactions —A reaction is said to be of zero order when the speed is proportional to the zero power of the concentration *i.e.* the reaction speed is constant and is independent of the concentration. Thus the reaction, bromination of acetone according to the equation,

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$$
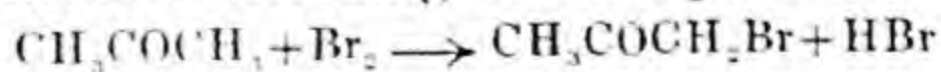
is said to be of zero order with respect to the reactant bromine since the reaction speed is not influenced by a change in the concentration of bromine within limits.

Not all reactions are of zero or integral order and many fractional order reactions are known. A very well-known and theoretically important reaction is the conversion of ortho-

hydrogen to para-hydrogen which is found .to be of $\frac{3}{2}$-order. Usually such order involves a mechanism where atoms or free radicals are intermediates.

Determination of the Order of a Reaction —The order of a reaction may be determined from experimental data in either of the following ways:—
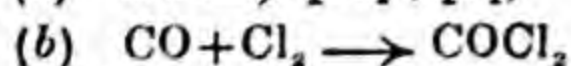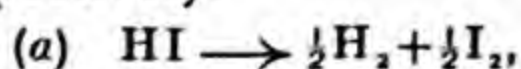
(a) APPLICATION OF THE FORMULA—The method consists in trying to fit all the equations for the different types of reactions with the collected data and in finding which of the equations gives the most concordant constant for the specific reaction rate, k. The method is laborious and sometimes the reactions are too complicated to yield a satisfactory constant with these simple equations.

(b) METHOD OF EQUIFRACTIONAL PARTS—It is often convenient to determine the time required to complete a given fraction, say, half of the total reaction for different initial concentrations. This 'half decomposition period' should be a constant for a first-order reaction and inversely proportional to the concentration for a second order reaction and so on, for reactions involving equal initial concentrations of the reactants.

(c) METHOD OF GRAPHING—For first order reactions if logarithms of concentration are plotted against time (i.e., $\log c$ against t), straight lines are obtained (Fig. 100). For second order reaction, straight lines are obtained by plotting graphically reciprocal of concentration ($1/c$) against time, and for third order reactions by plotting $1/c^2$ against time.

(d) METHOD OF ISOLATION—This consists in varying the concentration of one of the reactants and studying its effect on the reaction speed while the concentrations of the other substances are kept very large so that they do not sensibly vary during the course of the reaction. Thus the reaction, $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$, is termolecular since the speed is proportional to the concentration of stannous chloride when the ferric chloride is in large excess and is proportional to the square of concentration of ferric chloride when the stannous salt is in large excess. The method has recently fallen in disrepute, since it has been shown that the speed variation in presence of large concentrations of other substances, particularly electrolytes, may be quite different from the normal behaviour.

Mechanism of Reactions -As pointed out in the introduction it is frequently observed that the chemical equations are not in agreement with the kinetic order of the reactions. Thus, the following reactions are all found to be kinetically bimolecular though in the chemical equations represented in their simplest forms they appear to be uni-, bi-, ter-, and tetramolecular respectively.

(a) $HI \longrightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$,

(b) $CO + Cl_2 \longrightarrow COCl_2$

21

(c) $Ba(OH)_2 + 2CH_3COOC_2H_5 \longrightarrow (CH_3COO)_2Ba + 2C_2H_5OH$

(d) $2HgCl_2 + H_3PO_3 + H_2O \longrightarrow 2HgCl + 2HCl + H_3PO_4$
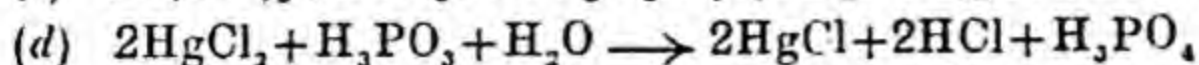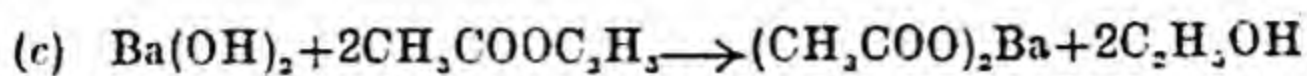
The explanation of this is that a chemical equation represents the over-all reaction which is composed of a number of consecutive steps the slowest of which determines the observed reaction speed. Thus, in reaction (d) of the previous list the first step is a bi-molecular slow reaction represented by

$$HgCl_2 + H_3PO_3 \longrightarrow HgCl + H_2PO_3 + HCl$$
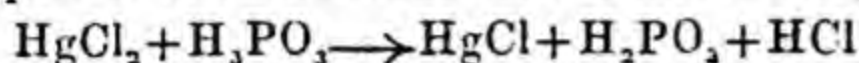
followed by the extremely rapid reaction,

$$2H_2PO_3 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

and so, the observed effect is that of a bi-molecular reaction.

Another very well-studied case of reaction mechanism is the *decomposition of hydrogen peroxide catalysed by halogen ions*. In the presence of say, iodide ion the reaction proceeds through the following stages—

$$H_2O_2 + I^- = H_2O + IO^-; \quad IO^- + H_2O_2 = H_2O + O_2 + I^-$$
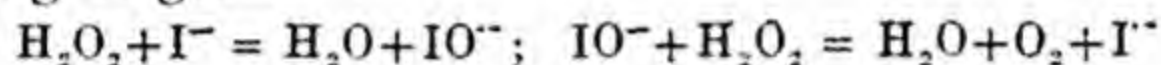
The first stage which is the slower reaction determines the reaction speed, since the second stage is dependent on the first one for the supply of IO^- ions. It is interesting to find that IO^- ions are produced by the first reaction and consumed by the second reaction and hence, after a small initial period it maintains a small but constant concentration throughout. Similar small but constant concentration of one of the comparatively unstable intermediate products is characteristic of many reactions and such a condition is called a *stationary state*.

A recent result of great interest in which reaction kinetics has played an important role, is the discovery that in nitration of benzene and similar compounds by HNO_3-H_2SO_4 mixture, the nitronium ion NO_2^+ is the real nitrating agent as shown below.

$$2H_2SO_4 + HNO_3 \rightleftharpoons 2HSO_4^- + H_3O^+ + NO_2^+$$

$$C_6H_6 + NO_2^+ \longrightarrow C_6H_6NO_2^+ \longrightarrow C_6H_5NO_2 + H^+$$
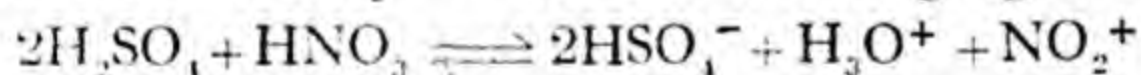
The mechanism of many reactions has been established by kinetic studies.

Chain Reactions—As postulated above, most reactions are the result of a number of consecutive reactions. An interesting case is the combination of hydrogen and chlorine in presence of a small concentration of chlorine atoms introduced by illumination or by some other process. A fast reaction immediately takes place according to the following scheme—

(a) $Cl + H_2 = HCl + H$;

(b) $H + Cl_2 = HCl + Cl$: a & b; and so on.
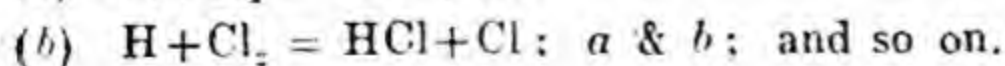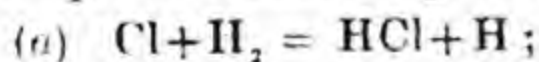
A chlorine atom is consumed in the first reaction and is produced in the second reaction and the cycle repeats itself continuously producing a reaction chain: and as many reaction chains are started as there are chlorine atoms. A reaction caused by a series of such successive processes is known as a *chain reaction*.

Such chains are initiated not only by atoms but also by free radicals or even energy-rich molecules. Chain reactions are of great importance for reaction kinetics, because many types of chemical reactions including explosions involve a chain mechanism.

Complex Reactions—Commonly occurring reactions do scarcely conform to the ideal types hitherto described. Conditions are generally more complicated due to the presence of (a) counter or opposite reactions (b) consecutive reactions (c) side reactions, and (d) period of induction, and due allowances are to be made for these disturbing influences.

Period of Induction—Some reactions seem to have a period of induction i.e. a short period at the initial stages when the reaction seems to be almost at a standstill and it goes on with normal speed after this period. The first observed case is the reaction between hydrogen and chlorine in the presence of sunlight to form hydrochloric acid. Such induction or inhibition period is very common in photochemical and polymerization reactions and is often due to the presence of negative catalysts as impurities which are being destroyed during the induction period.

Influence of Solvent on Reaction Speed—The classical study is by Menschutkin (1887) who studied the kinetics of the quaternisation reaction, say, between trimethyl amine and methyl iodide to form the quaternary ammonium iodide

$$(CH_3)_3.N + CH_3I \longrightarrow [(CH_3)_4N]^+I^-$$
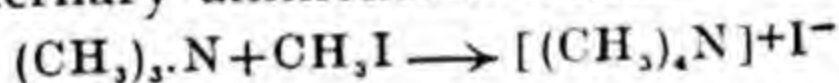
in a large number of solvents, and observed that a more than thousand-fold change of speed could be brought about by a change of solvent. A more thorough study has been lately made by Soper (1931) of the reaction between ethyl alcohol and acetic anhydride to form ethyl acetate in various solvents. Some of his results along with those of Menschutkin are given in the following table.

Solvent	Triethyl amine and ethyl iodide at 100°C; k_2	Acetic anhydride and ethyl alcohol at 50°C; k_2
Hexane	0·0119	0·00018
Benzene	0·0046	0·0058
Chlorobenzene	0·0053	0·023
Anisole	0·0029	0·040
Benzyl alcohol	—	0·133

A satisfactory explanation of these observations is yet lacking though it has been suggested that dielectric constant is an important factor in influencing reaction speeds. Any such simple theory is however evidently untenable. It is remarkable however that the speed of N_2O_5 decomposition is nearly the

same in a number of solvents and is almost equal to the rate of decomposition of N_2O_5 in the gaseous state.

Effect of Temperature on Reaction Speed: Energy of Activation —The speeds of almost all reactions are increased by a rise of temperature. This enhancement of speed is somewhat different for different reactions, but generally, the speed increases between two-to three-fold or even slightly higher for a rise of temperature of 10°C.

The following empirical equation first suggested by van't Hoff and verified by Arrhenius has been found to represent satisfactorily the variation of reaction speed with temperature for many reactions. Arrhenius' equation is

$$k = Ze^{-E/RT} \tag{8-XX}$$

where k is the velocity constant at the absolute temperature T, and Z and E are constants, E being called the *energy of activation*. The above equation implies (which can be easily shown by taking l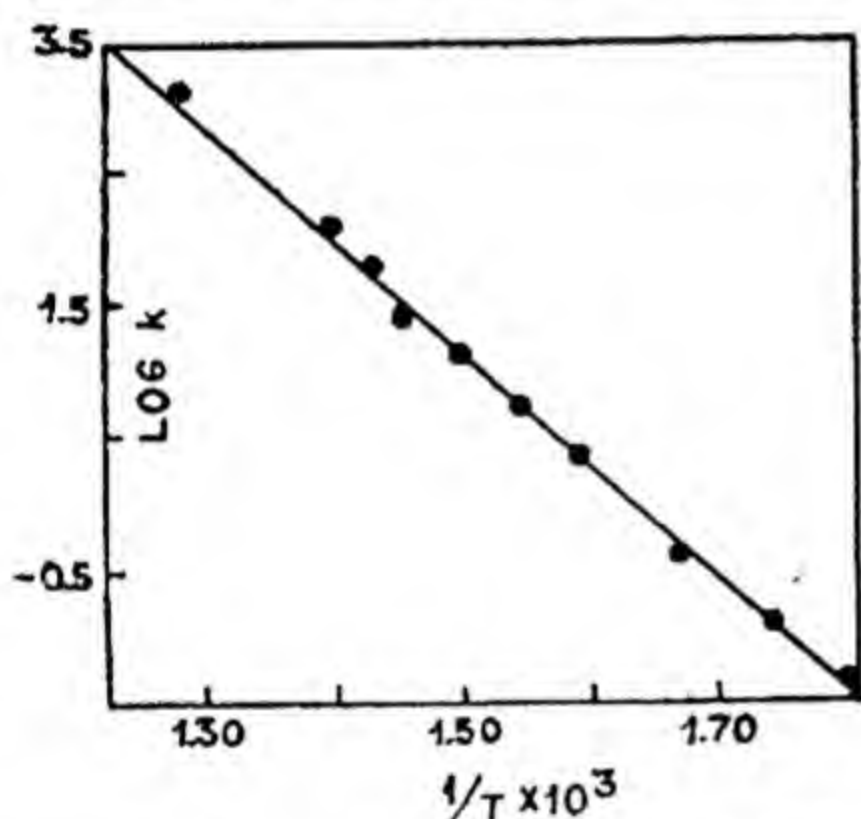ogarithm of both sides) that log k of any reaction gives a straight line when plotted against 1/T (Fig. 101). Further, it leads to the inference that other things being equal, a large energy of activation signifies a low reaction rate but at the same time a high temperature coefficient of the reaction. Further, in reactions in which primary bonds are ruptured or created, the energy of activation, E usually lies between 20,000 and 60,000 calories per mole.

Fig. 101—Linearity of log k vs 1/T (N_2O_5 decomposition) (Slope is proportional to E)

The above equation has got a formal analogy with the equation representing the variation of equilibrium constant with temperature [eqn. (18)-XIV], and hence the applicability of such an equation is judged as an evidence for the existence of an equilibrium between active and passive molecules in any reaction mixture.

THEORY OF REACTION RATE

Preliminary considerations —The ultimate aim of a theory is to predict for any reaction the value of its Z and E [equation (8)]. The current theories are far short of this goal. Two kinds of theoretical approaches are made to interpret the experimental values of Z and E. They are respectively called *collision theory* which is based on kinetic theory, and the theory of absolute reaction rate (also called the *transition state theory*) which latter

is based on quantum mechanics, and we shall discuss them very briefly in the next sections.

It should be pointed out here that the rate of a reaction has no connection with the position of equilibrium, *i.e.* free energy decrease of the system. For example, when an optically active compound racemises, the standard free energy change is the same for all racemization reactions, because an equimolecular mixture of dextro and laevo is formed at equilibrium, but the speed of racemization is very different for different compounds. So a thermodynamic approach to reaction rate does not seem to offer much prospect of success, and evidently we have to find out some other factor which determines the rate of a reaction.

The Collision Theory of Reaction Rate—If we calculate from kinetic theory the total number of collisions taking place per second in a gas decomposing at a measurable speed and also the total number of molecules decomposing per second, it will be found that the former is in far excess of the latter. That is, all collisions in such a gas do not lead to chemical reactions but only a small fraction of them is effective in this sense. Hence, simply molecular encounters do not cause chemical reactions, but some further conditions must be fulfilled. The question naturally arises what is this additional impetus which actuates some molecules in a given sample to decompose in any given interval while others do not, though they are undoubtedly chemically identical.

The clue to this enigma is suggested by the kinetic theory according to which all the molecules in a gas though they are chemically identical are not physically so. They differ widely among themselves in speed and hence, in kinetic energy content. Chemical change takes place in only those collisions which occur between molecules having relative kinetic energy in excess of a certain critical amount. This critical amount of energy necessary for chemical transformation of molecules calculated per mol is called the *energy of activation*, E for the reaction and molecules endowed with energy greater than this value are called 'activated' molecules.

The value of the fraction of collisions involving molecules endowed with energy greater than E is found from kinetic theory to be equal to *exp* $(-E/RT)$. If the total number of collisions in a gas at unit concentration be Z, evidently the number of molecules decomposing per second, which is equal to k, will according to collision theory be given by the following equation.

$$k = Ze^{-E/RT} \qquad \qquad \dots (9)\text{-}XX$$

where Z is called the *frequency factor* and E is the *energy of activation*. Thus we have been able to deduce equation (8), the general equation for reaction rate, from collision theory.

Transition State Theory —According to this theory the reactants say AB and C first form a transition complex A......B......C, which then decomposes into A and BC

$$AB + C \underset{}{\rightleftharpoons} A..B..C \longrightarrow A + BC$$
(*reactants*)   (*transition complex*)   (*resultants*)
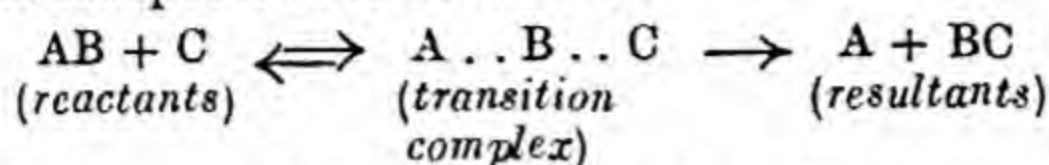
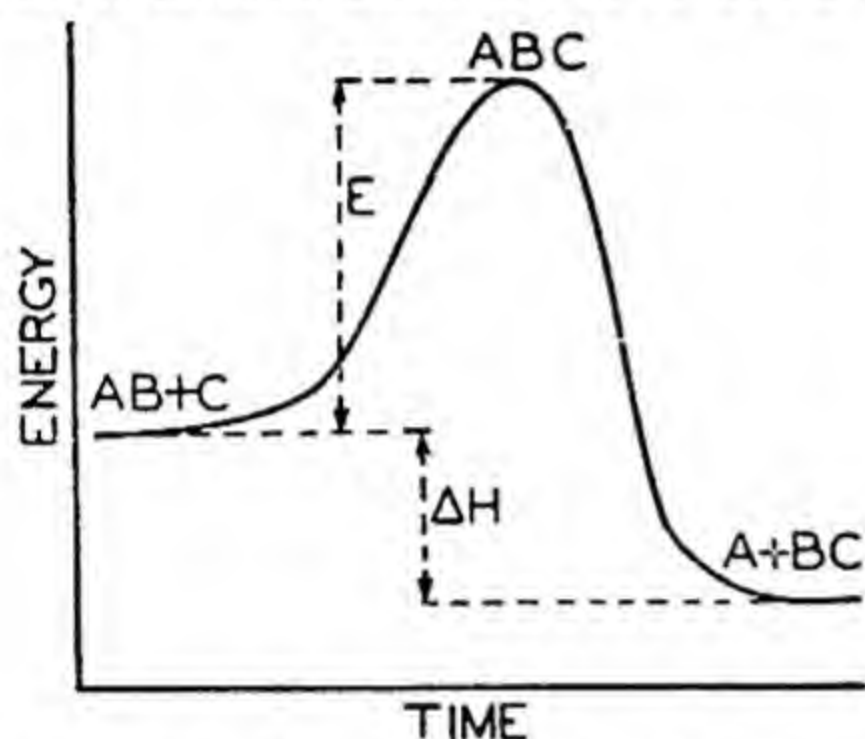The basic idea is that we must somehow force C to come so clsoe to B that B becomes undecided as to which atom it now belongs. This state of indecision as to B being attached both to A and C, though somewhat loosely than before, is the *transition state*, also called the *activated complex*. The energy necessary to push C to approach B to create this transition state or activated complex is the energy of activation, E. Fig. 102 graphically describes the energy barrier created by the formation of the transition complex. We have, as it were, to roll the reactants over this energy hill of the transition state to the valley of the products.

Fig. 102—Physical Representation of Energy of Activation

A crude physical analogy of the energy of activation may help to clarify the concept. To roll a ball from one valley to another, the ball has to be taken to the top of the hill separating the two valleys. The difference in level between the two valleys corresponds to the heat of reaction, while that between a valley and top of the intervening hill, the energy of activation. Fig. 102 is a graphical representation of such a mechanism for the reaction, AB+C ⟶ A+BC.

This is amenable at least in principle to mathematical analysis with the help of quantum mechanics and an equation similar in form to equation (8) is obtained. To go into any more details would be much beyond the scope of the present book but it may be remarked that this approach has found more favour and is being much refined and developed to embrace a larger number of reactions.

Exercises

1. Deduce the expression for the velocity co-efficient of a bimolecular reaction. How would you distinguish between a unimolecular and a bi-molecular reaction.

2. Explain the term "velocity constant" and "order of chemical reaction."

3. Write short notes on :—(*a*) Order of a reaction. (*b*) Uni-molecular reaction. (*c*) Heat of activation, (*d*) Biochemical catalysis.

4. If one per cent decomposes in the first minute in a unimolecular reaction, calculate how much would decompose in the first hour.   [54·4%]

5. If $k_1 = k_2 = k_3$ for three reactions being respectively uni-, bi-, and ter-molecular, when concentration is expressed in mols/litre, what will be the above relation if the concentration unit is mols/c.c.

6. If 100 gms. of A be present in a solution and x gms. decompose in one hour, how will this amount decomposed in one hour change on dilution of the original solution to twice its volume in case the reaction is of (*i*) first order, (*ii*) second order or (*iii*) third order.

7. If k is the same for three reactions of first, second and third order respectively (unit of c=mols/litre), which reaction should be the fastest? Is this true for all ranges of concentration? Discuss.

CHAPTER XXI

CATALYSIS

Introduction—In 1835 Berzelius drew attention to the fact that the speed of a number of reactions was enhanced by the mere presence of a foreign substance, which did not apparently take part in the chemical reaction. *Berzelius* believed that this was due to some kind of mysterious force, and named the phenomenon *catalysis*, and the substance thus influencing a chemical reaction, a *catalyst*. We are familiar with a large number of catalytic chemical reactions, *e.g.* the decomposition of $KClO_3$ catalysed by MnO_2, inversion of cane sugar to glucose and fructose catalysed by acids, combination of hydrogen and oxygen catalysed by finely divided platinum, etc. Ostwald defines a catalyst as a substance *which influences the speed of a chemical reaction but itself remains unchanged in mass and composition at the end of the reaction.*

Homogeneous Catalysis—The name applies to cases where *all the substances are present in one single phase.* Classical examples of gaseous reactions of this type are (*a*) nitric acid vapour in the oxidation of sulphur dioxide (*chamber process*) and (*b*) traces of moisture in the combustion of hydrogen, carbon monoxide etc. Homogeneous catalysis in solution includes *acid-base catalysis e.g.* inversion of cane sugar catalysed by acids, and hydrolysis of methyl acetate catalysed by both acids and bases, etc.

Heterogeneous Catalysis—The name applies to catalysis *where the catalyst forms a separate phase, usually a finely divided solid, and the reacting substances are gases or liquids.* The most common type of heterogeneous catalysis, *viz.* a solid catalyst either as such or supported on an inert solid such as asbestos, when used to catalyse a gaseous reaction, is often styled as *contact catalysis.* This kind of catalysis is of great technical importance as it is involved in most technical gas reactions.

Some notable examples are (i) finely divided platinum or vanadium penotoxide in the *contact process* for the oxidation of SO_2 to SO_3. (ii) reduced iron alone or with promoters, platinum, uranium, etc. in *Haber's process* for synthesis of ammonia, (iii) powdered iron in mixture with Ni, Co and oxides of Mg, Mn and Th in the *Fischer-Tropsch process* for manufacture of liquid hydrocarbons from a mixture of CO and H_2 (water gas), (iv) finely divided nickel for *hydrogenation of vegetable oils* such as groundnut oil, cotton seed oil, etc. to semi-solid products (Vegetable ghee or Vanaspati), etc.

Recently it has been shown that many gaseous reactions, *e.g.* decomposition of phosphine, arsine, etc. which were believed to be homogeneous are really heterogeneous reactions occurring

catalytically on the *surface* of the containing vessel and so, they are sometimes called *wall-reactions* (P 314).

Types of Catalysis—Catalytic reactions are conveniently classified into four types (*a*) *positive catalysis,* (*b*) *negative catalysis,* (*c*)*auto-catalysis and* (*d*) *induced catalysis.*

(*a*) **Positive Catalysis**—This type of catalysis includes those reactions in which the speed of the reaction is *increased* by the presence of the catalyst. The term catalysis was originally applied in this sense only, and all examples already given are of this type.

(*b*) **Negative Catalysis**—When the catalyst retards the speed of a chemical reaction, it is called a *negative catalyst, a retarder* or an *inhibitor*. Examples of this type are:—glycerol retaring the oxidation of sulphite by air; alcohol retarding the oxidation of chloroform to poisonous phosgene gas; hydroquinone stabilizing vinyl compounds which otherwise polymerize, etc.

The importance of negative catalysis in technology is enormous. Unstable chemicals are preserved by negative catalyst, *e.g.* a trace of hydroquinone stabilizes monomers; acetanilide or barbituric acid preserves hydrogen peroxide; sodium benzoate is used as a food preservative, and *corrosion inhibitor,* etc. An important type of negative catalyst is classed as *anti-oxidants* which are of great technical importance for rubber, food, plastics, petroleum and oil industry and billions of rupees worth are manufactured annually. Thus, aromatic amines are used as antioxidants for prolonging the life of rubber, etc., but the widest technical application of negative catalysis is in the use of lead tetra-ethyl or iron pentacarbonyl as 'anti-knock' in motor fuel. It is nowadays believed that such reactions are *chain reactions* and negative catalysts retard the reaction by breaking a vital link in the chain.

(*c*) **Auto-Catalysis**—Some reactions proceed with *gradually increasing rapidity* due to the formation of a catalyst as a result of the chemical reaction. Thus hydrolysis of ester by water is auto-catalytic, since the acid liberated as a result of hydrolysis catalyses the reaction. A common example is the decolorisation of oxalic acid by permanganate, which is initially a very slow reaction but, after some time goes on fairly rapidly due to the formation of Mn^{++} ions, which catalyse the reaction.

(*d*) **Induced Catalysis**—Sodium arsenite solution is not oxidised by the oxygen of the air, but sodium sulphite is oxidised under the same condition. If air is passed through a mixture of sulphite and arsenite solution, both of them undergo *simultaneous oxidation,* though the arsenite is not oxidisable by any of the substances present in the system individually. These types of reactions are called *induced catalysis,* and is due to some transient active intermediate formed in the first reaction.

Criteria of Catalysis—(*i*) *A small quantity of a catalyst is sufficient to effect an appreciable change in the velocity of a reaction.* A well-known example to the point is the presence of minute traces of moisture indispensable for a number of reactions (*see* later). Another striking case is the influence of

copper salt in influencing the rate of oxidation of sodium sulphite solution by air, which is perceptibly enhanced by the presence of copper salt even at a dilution of 1 part in ten million litres.

(ii) *The catalyst remains unchanged in mass and composition* —Though there is no diminution in amount or any permanent change in chemical composition, still the physical state of the catalyst may be changed. Solid crystalline $KMnO_4$ when used to catalyse $KClO_3$ decomposition becomes disintegrated into a fine powder. Smooth platinum when used as a catalyst in the oxidation of ammonia becomes roughened and pitted on the surface after some use.

(iii) *Catalyst cannot start a reaction* —Ostwald believed that the catalyst can only accelerate a reaction which is already occurring very slowly. According to this view, hydrogen and oxygen are actually combining at room temperature, but so slowly that it is beyond detection ; the introduction of platinum catalyst only hastens this reaction. This view becomes plausible on the ground that hydrogen and oxygen do really combine with measurable velocity at high temperature, but with decreasing temperature the speed rapidly falls off. Ostwald compares a catalyst as a 'whip on a horse, or oil in a machine only decreasing the friction by proper lubrication.'

The other view holds that hydrogen-oxygen mixture at room temperature is a case of *'arrested' reaction* or *unstable equilibrium* and the catalyst does actually initiate the reaction to go to the state of true equilibrium. It is difficult to decide between these two opposite views, "which have been likened to a game in which the catalyst is either comparable to the crowd which cheers the players or is looked upon as an essential player without whom the game cannot proceed."

(iv) *The catalyst cannot alter the final state of equilibrium ; it influences the direct and the reverse reaction to an equal extent* —Since a catalyst is reproduced back after the reaction, and so does not supply any energy to the system, it follows from thermodynamics that it will have no effect on the true equilibrium point: its only effect will be to reach the same equilibrium point in a shorter time. This point has been experimentally tested for various reactions. For example, it has been found that at the same temperature the yield of sulphur trioxide is the same, whether the catalyst used be platinised asbestos, ferric oxide or vanadium pentoxide.

Since a catalyst has no influence on the final state of equilibrium, it follows that the equilibrium constant, K is independent of the catalyst. But $K=k_1/k_2$ *i.e.* K is the ratio of the two velocity constants. If the catalyst changes any one of k_1 and k_2, the other will also change in the same proportion so that their ratio K remains the same (*vide* P. 210, eqn. 1).

(v) *Universality and specificity of catalytic action* —The phenomenon of catalysis seems universal and specific, since almost

all types of reactions are catalysed by suitable agents. For every reaction however, there is a most effective catalyst, which can be discovered only by trial and experiment.

Catalyst Poisons —It has been observed in many industrial catalytic processes, that the presence of minute traces of certain substances inhibits the efficiency of the catalyst and ultimately destroys the catalytic activity. These substances are called catalyst "poisons" or *anti-catalysts*. The most well-known catalyst poison is arsenious oxide, to remove which special care is taken in contact process. H_2S, CO. $HgCl_2$, etc. also act as catalytic poisons and peculiarly enough they are usually also poisonous to the organism. The poisons are perhaps strongly adsorbed on the active spots of the catalyst and thus reduce the extent of the catalytically active surface.

Catalyst Promoters —The addition of small amounts of foreign substances, which might not themselves be catalytically active sometimes enhances the activity of the catalyst. *The substances added to catalysts for increasing their activity are called* "promoters". The most efficient promoter action that has come to light is the use of aluminium oxide and alkali metal oxides in conjunction with reduced iron as catalyst in the synthesis of ammonia, the catalytic mixture having the composition $Fe + Al_2O_3 + K_2O$ (or Na_2O).

Water as Trace Catalyst —It has been reported by Baker (1894) and others that many reactions are totally stopped by intensive drying of the reactants ; a selection of some important ones is given below—

Solid solid reaction ..CaO. $CuO + SO_2$; $CaO + 2NH_4Cl$.

Solid gas reaction $P_2S_5 + O_2$; $CaO + CO_2$; $CaCO_3 + HCl$;
$NH_4Cl = NH_3 + HCl$; $H_2S + $salts.

Metalgas reactions $Na + Cl_2$; Na. $K + O_2$; Na. $Al + HCl$.

Gas reactions ..$H_2 + Cl_2$; $H_2 + O_2$; $NO_2 + O_2$; $(CN)_2 + O_2$;
$NH_3 + HCl$; $CO + O_2$.

Later workers however could not confirm all these findings. For example, Briner (1926) observed the brown coloration by the interaction of NO and O_2 even at liquid air temperature where the dehumidification by liquid air is at least as good as that by phosphorus pentoxide. Another striking example is the hydrogen-chlorine reaction. In a critical study of this reaction, Bodenstein (1933) concludes that no positive catalysis by water vapour is involved but on the contrary in the drying process traces of impurities are introduced into the gas phase which act as negative catalysts by breaking the reaction chain. Even Baker's claim of the inhibition of association and dissociation of ammonium chloride by intensive drying is contested by Bodenstein who attributes it to a removal through drying of condensation nuclei necessary for the solid salt deposition.

Many authorities however concede to the authenticity of the phenomenon at least in a few cases and attempts have been made to advance a common explanation based on dipole nature of water, or chain mechanism, or intermediate compound formation. It might be possible however that these apparently similar results are being effected by quite different causes and hence, every such reported reaction must be considered in its own right.

Types of Catalysts : Catalysts are nowadays classified on the basis of the reactions in which they take part. Thus, alumina is an efficient *dehydration catalyst* whereas nickel is a powerful *hydrogenation catalyst.* Some of the various types of industrially important reactions and catalysts are mentioned below:

Reaction	Example	Catalyst

(2) Hydration : $CH_2-CH_2+H_2O = CH_2-CH$ Silver Oxide

       O   OH   OH

    Epoxide   *Glycol*

(2) Dehydration : $C_2H_5OH = C_2H_4+H_2O$ Alumina, Zirconia
       Alcohols   *Olefines*

(3) Hydrolysis : *Oils+Water = Fatty acids+Glycerol* ZnO, CaO.
         (Glycerides)   Twitchell Reagent

(4) Hydrogenation :
     Olefines+H_2 = Paraffins   Nickel, Pt, Pd.
     Oils+H_2 = Fats
     $N_2+H_2 \longrightarrow NH_3$ Fe_2O_3/Al_2O_3, Cr_2

(5) Dehydrogenation :
     Ethyl Benzene = Styrene + H_2 Cr_2O_3/MoO_3

6) Oxidation :
     Benze+Air = Maleic Anhydride V_2O_5

(7) Alkylation :
     Benzene+alkyl halide, alcohol or $AlCl_3$, BF_3, HF
        olefine = paraffins

(8) Isomerisation : *n*-Paraffin $\longrightarrow$ Iso-paraffins $AlCl_3$

(9) Cracking :
     Long chain hydro- Short chain hydro-carbons Clay, Bauxite
     carbon molecules $\longrightarrow$ with branching at the chain MoO_3
                                             Pt/PtO_2

(10) Halogenation : Olefines+Cl_2 = Dichlorofines $SbCl_3$, $FeCl_3$

(11) Dehydrohalogenation :—
     Dihalo-olefines = Vinyl halide Al_2O_3, Active charcoal

(12) Polymerization : Ethylene $\longrightarrow$ Polythylene   Ziegler Catalyst

Mechanism of Catalytic Action—Fundamentally, catalysts often act by providing a reaction path that has considerably lower energy of activation than that of the uncatalysed path of reaction, and all mechanisms are aimed to find the details of this easier reaction path. Catalytic reactions are usually explained on the basis of either of the two theories, (*a*) Intermediate Compound Theory and (*b*) Adsorption Theory.

(*a*) *Intermediate Compound Theory*—This theory explains catalytic phenomena as due to the formation of unstable intermediate compounds of greater activity than the reactants. The classical explanation by Clement and Desormes (1806) of the mechanism of the oxidation of SO_2 by the catalytic influence of NO_2 may serve as a typical illustration of this type. The intermediate steps can be represented as—
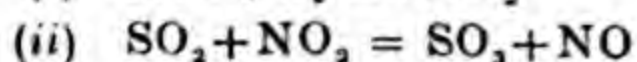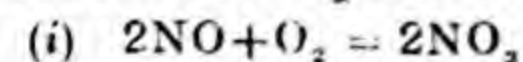
     (*i*) $2NO+O_2 = 2NO_2$
     (*ii*) $SO_2+NO_2 = SO_3+NO$
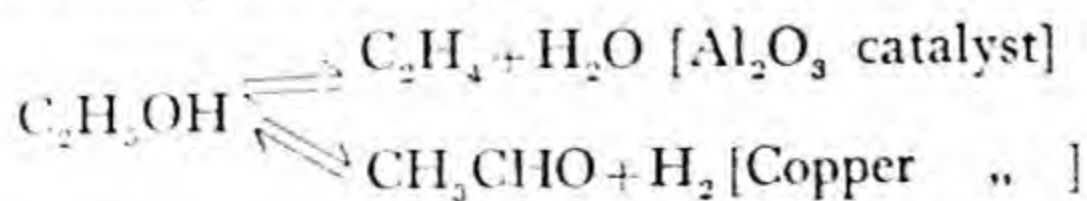   the net reaction being, $2SO_2+O_2 = 2SO_3$.

Similar explanations have been found to be true in the case of many organic reactions, the most familiar of which is the formation of ether from alcohol with sulphuric acid as catalyst, the intermediate compound being ethyl hydrogen sulphate as proved by Williamson. In Friedel-Craft's reaction, an intermediate additive compound of $AlCl_3$ and the acid chloride is generally assumed. Another thoroughly tested reaction mechanism of this type is the catalysed decomposition of H_2O_2 by iodide ions (P. 322).

However, the isolation of a compound does not necessarily prove it to be the intermediate fugitive complex, neither the inability towards isolation disproves the theory. In fact, the intermediate compound would be an unstable one, capable of readily undergoing further changes in the environment concerned and this may explain the failure to isolate such compounds in many cases.

(b) *Adsorption Theory*—According to this theory it is assumed that the reacting substances are adsorbed on the surface of the catalyst where the close proximity of the adsorbed molecules is responsible for the chemical reaction. This theory was first suggested by Faraday to explain the catalytic combination of hydrogen and oxygen by platinum and has been accepted with modifications by almost all recent workers.

It is believed that on the surface of solid catalysts there are some isolated *active spots* where due to the *residual affinity* of the solid surface, molecules from the gas phase are adsorbed which react and then fly off leaving the surface free for fresh action. High concentration of the gases in the adsorbed layer is only one of the factors for increased activity. When two molecules collide and react, the heat of reaction remains in the resulting molecule, which if not deprived of this energy by fresh collision automatically breaks down again. It is believed that the catalyst surface renders positive help in *draining out this excess energy*. Apart from these general effects *specific chemical forces* at the interface are generally assumed to have some part in the play by smoothing the path of the reaction by *lowering the energy of activation* necessary for the process.

That specific chemical forces come into play in contact catalysis can be illustrated by the influence of different catalysts upon the decomposition of ethyl alcohol. For example, an alumina catalyst forms chiefly ethylene and water, whereas copper catalyst gives mainly acetaldehyde and hydrogen.

$$C_2H_5OH \begin{array}{c} \nearrow C_2H_4 + H_2O \ [Al_2O_3 \ \text{catalyst}] \\ \searrow CH_3CHO + H_2 \ [\text{Copper} \quad ,, \quad] \end{array}$$

That Al_2O_3 is an electron-poor substance and so tends to attach itself to the oxygen atom of the adsorbed alcohol, whereas the

electron-rich copper donates electron to hydrogen. may be the specific chemical forces which come in play.

These two theories are not incompatible with each other. In fact, *the loose adsorption compound* of the adsorption theory and the *unstable intermediate compound* of the other theory are, in essence, the same though clothed in different languages to suit different view-points.

Biochemical Catalysis: Enzymes—Certain substances called enzymes occurring in some natural juices, plants, etc. possess the incredible capacity of bringing about many complex chemical reactions, such as, hydrolysis, oxidation, reduction, etc. They are large proteinaceous molecules and their action is mainly catalytic in so far that they do not take part in the chemical change and a small quantity of the enzyme suffices to bring about the decomposition of a large quantity of the *substrate i.e.* the substance on which the enzyme acts. Some very well-known examples of enzyme action are the enzyme *zymase* present in yeast which is responsible for alcoholic fermentation of glucose to alcohol, the enzyme *urease* present in soya bean which converts urea into ammonium carbonate, the enzyme *pepsin* and *trypsin* present in the gastric juice and the pancreatic juice respectively which help the digestion of food, etc. Ferments, enzymes, hormones, vitamins, etc. are all examples of biochemical catalysts.

About the kinetics of enzyme action, it is generally observed that the reaction speed is proportional to the concentration of the enzyme and that the rate of disappearance of the substrate follows a unimolecular or logarithmic course for low concentration of the substrate but sometimes with the progress of the reaction the speed becomes slower. For high concentration of the substrate if the enzymes are in no way hampered in their activity by the products of reaction or by other factors, the amount of decomposition per unit time remains sensibly constant throughout, the reaction thus appearing null-molecular or of zero order. It is believed that the reacting molecules are adsorbed on the giant (colloidal) enzyme molecules where they react, and the products of reaction then diffuse out leaving fresh space for further adsorption. Evidently, such a mechanism of enzyme action has a formal resemblance with heterogeneous catalysis, and the falling off of the rate is explained on this theory as due to the gradual blocking of the active spots of the enzymes by adsorption of the products of reaction.

Enzyme action is, however, differentiated from catalysis in some important respects. Most enzyme reactions have got an optimum working temperature, often the blood temperature of mammals, below or above which the reaction speed rapidly falls off. The enzymes often require the company of some smaller molecules, called *coenzymes,* which may be inorganic ions or adenosine diphosphate or triphosphate, to be fully effective.

The enzymes are very specific in their action ; the enzyme decomposing cane sugar may not decompose malt sugar. The reactions brought about by enzymes are often inhibited by small quantities of extraneous matters usually classed as poisons, and they generally require a definite range of acidity (*i.e.* narrow limits of *p*H) beyond which all action ceases. Previously some mystery surrounded the enzymes, but recently they have been proved to be definite chemical individuals quite a few of them having been isolated in the pure crystalline form.

IMPORTANCE OF ENZYMES IN SCIENCE AND INDUSTRY. —Organic metabolism, the conversion of food into energy and structural molecules by living matter, is a series of enzyme reactions and hence, their study is of vital importance to the science of biology and medicine. Industry also owes a great deal to the activity of the enzymes or ferments as they are ordinarily called. Besides the familiar manufacture of wine, vinegar, curd, cheese, etc., by fermentation process, butyl acetate and amyl acetate, the two main solvents for nitrocellulose lacquers and varnishes are products of fermentation industry in the sense that their intermediates, butyl alcohol, amyl-alcohol and acetic acid along with many more *viz.* acetone, lactic acid, etc. are all produced by fermentation.

Exercises

1. Explain with illustrations :—(*a*) Catalysis (*b*) Negative catalysis.

2. What are catalyst poisons and promoters.

3. Discuss some commercially important catalytic processes?

4. Give a brief account of the various theories that have been put forward to explain the phenomenon of catalysis.

5. Explain the principal features of catalytic action. Write short notes on the industrial uses of any two of the following catalysts : iron, nickel, platinum and vanadium pentoxide.

PART V

SURFACE CHEMISTRY

Adsorption and other interfacial phenomena—Colloid chemistry.

CHAPTER XXII

ADSORPTION & OTHER INTERFACIAL PHENOMENA

Introduction— If a piece of cocoanut charcoal is introduced into a closed space containing say, ammonia gas, it is observed that a good quantity of ammonia is quickly taken up by the charcoal. Not only ammonia but almost all gases are thus taken up by charcoal to a more or less degree.

It can be proved experimentally that the gas which is thus taken up remains on the surface of the charcoal, and does not go into the interior of the solid. The simplest proof of this is that if the same sample of charcoal is more finely divided to produce greater surface area per unit mass, it can take up more gas. *This process of accumulation of any substance* (here, gas) *on the surface of another substance, is called* **adsorption.** Hence adsorption is a surface phenomenon and as such, is a fairly rapid process. Strong adsorption is connected with a large surface and so all good adsorbents are solids in a very finely divided state. Not only gases but also liquids and substances in solution can be adsorbed by suitable adsorbents. An example of the last type is met with in decolorising sugar solution with charcoal.

Adsorption is generally distinguished from **absorption,** which involves an actual penetration of the substance into the interior of the material doing the sucking. Hence it is a rather slow process. Of course, in many cases, the initial rapid adsorption is followed by a slow process of absorption of the substance into the interior of the solid. Many authors, nowadays, use the term **'sorption'** to denote any process of taking up of a substance by a porous solid.

Charcoal and other solids gain increased power of adsorption on heating at low pressures with various gases or in a vacuum at temperatures varying from 400° to 1000°C. Such treated charcoal is called *activated charcoal* and this process of augmenting the power of adsorption is called *activation.* The simplest explanation of activation seems to be that the hydrocarbon and other impurities present in the carbon are distilled off leaving an extra surface which gets activated by reaction with the activating gas.

Nomenclature— The material upon whose surface the concentration takes place is called the **adsorbent** (*e.g.* charcoal in the above example), the substance which is taken up on the surface is called the **adsorbate,** and the common surface between the two phases where the adsorbed molecules concentrate is called the **interface.**

Characteristics of Adsorption.— The most general feature of the process of adsorption is that it is *selective and specific.* In other words, to what extent a certain substance will be adsorbed

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by an adsorbent depends on the physical and chemical nature of both the adsorbent and the adsorbate, and it is not possible to predict the extent of adsorption in any combination. However, it is generally observed that *easily liquefiable gases are more easily adsorbed.*

Effect of Temperature—A gas is generally the more adsorbed the lower the temperature. This is illustrated by the following table for *activated* cocoanut charcoal.

Gas	Vol. of gas absorbed by 1 cc charcoal	
	0°C	—85°C
Argon	12	175
Oxygen	18	250
Carbon monoxide	21	190
Nitrogen	15	155
Hydrogen	4	135
Helium	2	15

Since the amount of adsorption falls off with increasing temperature, it follows from Le Chatelier's theorem that the adsorption of a gas is an exothermic process. The heats of adsorption have been measured in many cases and have been found to vary from system to system and to range from about 4,000 to 60,000 calories per mol.

Effect of Pressure and Concentration—An increased pressure of a gas or vapour, or an increase in the concentration of a solute causes increased adsorption. The increase of adsorption with increased pressure is experimentally found not to be proportional to pressure but is somewhat less and so, Freundlich puts the adsorption proportional to a fractional power of pressure, and the resulting equation which gives the relationship between the amount adsorbed and the pressure is known as **Freundlich adsorption isotherm.**

$$\frac{x}{m} = k \, P^{\frac{1}{n}} \quad \text{or} \quad \left(\frac{x}{m}\right)^{n} = kP \qquad \ldots \quad (1)\text{-XXII}$$

where x is the amount adsorbed by m gms of adsorbent at pressure P; k and n are constants for any given combination at any given temperature. This equation is an approximate one and does not hold good over a wide range of pressure.

The same equation of Freundlich approximately describes the behaviour of adsorption from solution, with the difference that instead of pressure P we have to use concentration c. Thus, the equation becomes,

$$\left(\frac{x}{m}\right)^{n} = kc \qquad \ldots \quad (2)\text{-XXII}$$

Taking logarithm of both sides, we get

$$n \log \left(\frac{x}{m}\right) = \log k + \log c. \qquad \ldots \qquad \ldots \quad (3)\text{-XXII}$$

This shows that if the logarithm of the amount adsorbed per unit mass of charcoal is plotted against the logarithm of the final concentration of the substance adsorbed, a straight line will be obtained. This is only roughly true in most cases.

Two Types of Adsorption— It is generally believed that two kinds of force are operative in adsorption processes. The first kind is a weak type of force called van der Waals force and this is responsible for what is known as *physical adsorption* which has a heat of adsorption of the order of 10,000 calories. The other type of force which is much stronger is considered to be chemical in nature and the adsorption caused by the play of such forces is called *chemisorption or activated adsorption*. This latter type of adsorption has much higher heat of adsorption usually ranging from 20,000 to 60,000 calories. It is however very often not possible to distinguish these two extreme types as both types of adsorption simultaneously occur in most actual cases. A typical example of physical adsorption is that of nitrogen on mica and of the other type is the well-known adsorption of oxygen by tungsten which was shown by Langmuir to lead to a virtual formation of a layer of oxide of tungsten on the surface.

Distinction between Physical Adsorption and Chemisorption —The intermolecular attraction responsible for physical adsorption is essentially the same which causes condensation of a gas to the liquid state as also capillary condensation. Since high boiling point means strong intermolecular attraction, adsorbate of higher boiling point undergoes greater physical adsorption under otherwise identical conditions.

Another distinguishing characteristic is that physical adsorption is nonspecific whereas chemical adsorption involves a high degree of specificity like chemical forces. The forces responsible for chemisorption is, therefore, much stronger and so, chemical adsorption is irreversible or reversible with great difficulty. For example, ethyl alcohol vapour adsorbed on finely divided nickel is recovered not as ethyl alcohol but as a mixture of $CH_3CHO + H_2$; oxygen chemisorbed on tungsten is pumped off largely as tungstic oxide; protein if adsorbed on charcoal and recovered is found in a denatured state. Very often for the same adsorbent-adsorbate system physical adsorption predominates at low temperature and chemisorption at higher temperature because chemisorption has a very slow rate at low temperature *i.e.* it has a fairly large energy of activation.

The most common adsorbent, charcoal, acts both by physical adsorption sometimes leading to capillary condensation, and also by chemisorption. Oxygen adsorbed on activated charcoal is

recovered considerably as oxides of carbon, which proves the chemisorption of oxygen on charcoal.

Langmuir's Theory of Adsorption– Langmuir (1916) considers the process of adsorption as due to an equilibrium between the adsorbed and the unadsorbed gas. Langmuir imagines that a gas molecule on striking a surface gets condensed there (this is called *inelastic collision*) and evaporates off only after an appreciable time, and this *time lag between condensation and evaporation* causes adsorption. His another premises which evoked great controversy and discussion, is that *the adsorbed layer is normally only one molecule thick* though he concedes that under some circumstances polymolecular layers (*i.e.* a layer more than one molecule thick) can be built up.

The adsorption isotherm can be deduced after Langmuir as follows :— Let μ be the number of molecules of a gas hitting per unit surface area of the adsorbent in one second and let a constant fraction say, α of it adhere to the surface. Then the number of molecules condensing per unit area per sec. is $\alpha\mu$. If θ be the fraction already covered up with the adsorbed gas, then $(1-\theta)$ fraction of the surface is free and so the number of molecules condensing per second $= \alpha\mu(1-\theta)$. The rate of evaporation however, is proportional to the area already covered up by the molecules and hence the total number evaporating per sec. is $\gamma\theta$ where γ is a constant. At equilibrium, the rate of evaporation is equal to the rate of condensation, *i.e.*

$$\gamma\theta = \alpha\mu(1-\theta) \qquad \therefore \ \theta = \frac{\alpha\mu}{\gamma+\alpha\mu}$$

Now θ is proportional to the quantity of the gas adsorbed, say x, and μ to gas pressure, p; hence we get Langmuir's equation,

$$x = \frac{ap}{1+bp} \quad \dots \ (4a) \qquad \text{or} \quad \frac{p}{x} = \frac{1}{a} + \frac{b}{a}\,p \qquad \dots \ (4b)\text{-XXII}$$

where a and b are constants. Eqn. $4a$ is known as Langmuir equation.

This equation agrees very well with experiments as shown by the following table compiled from Langmuir's data. Fig. 103 shows the same data as the amount adsorbed (x) versus *pressure*

ADSORPTION OF NITROGEN ON MICA

	Pressure, p (bars)	x (observed)	x (calculated)
Temp = 90° K	34·0	33·0	32·8
$a=0·156$	17·3	28·2	28·4
$b=38·9$	9·5	23·9	23·2
	6·1	19·0	19·0
	4·0	15·1	15·0
	2·3	12·0	11·8

(p) curve. Fig. 104 shows the same data plotted as p/x against p, and this is found to be linear in agreement with the Langmuir equation. For high values of μ, Langmuir equation tends to

reduce to Freundlich's equation, which is therefore only a particular case of Langmuir's equation.
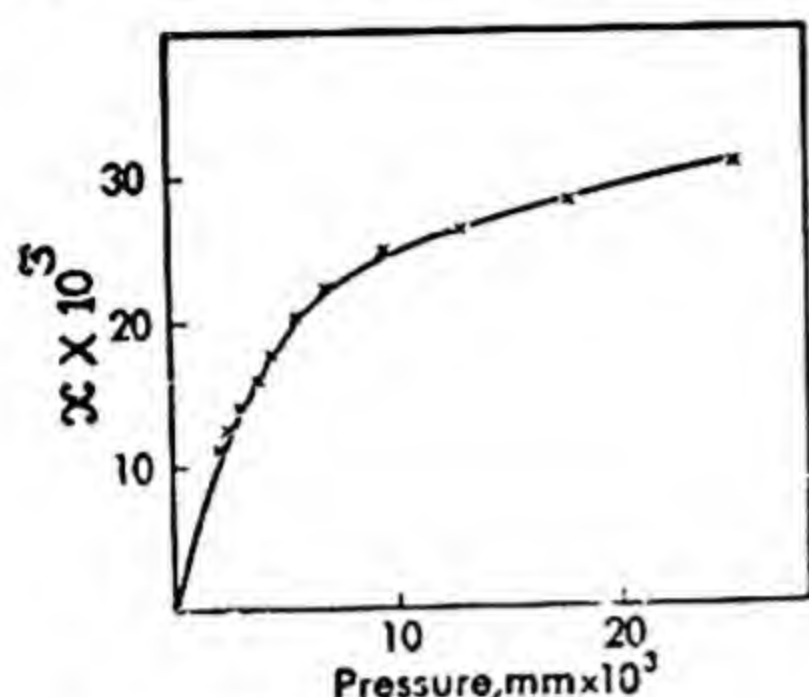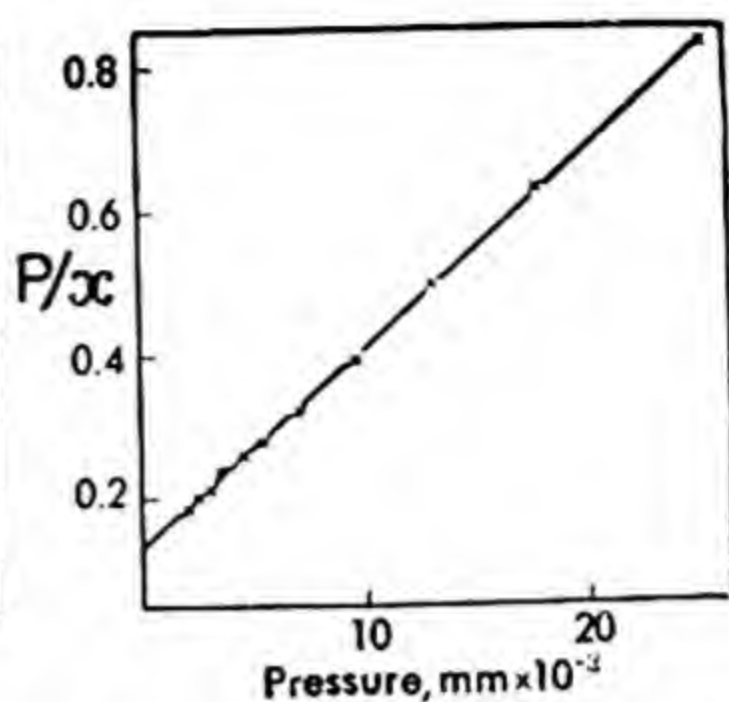

Fig. 103—Adsorption and Pressure

Fig. 104—Langmuir's Plot of Adsorption Data

However, Langmuir's equation very often fails at higher pressures, and it is nowadays believed that in contradiction to Langmuir's idea of unimolecular layer, multimolecular layers are built up owing to intermolecular attraction of the same type as causes gas molecules to condense (physical adsorption). Equations based on such ideas of *multilayer adsorption*, specially one called B. E. T. equation, have been lately derived which give somewhat better agreement with experimental data.

Orientation at Interface— The credit of Langmuir does not lie so much in the deduction of the above equation as in affording a plausible picture of the process of adsorption. According to Langmuir's view, the adsorbed molecules are attached to the surface by a bond chemical in origin, as a result of which they do not remain adsorbed in a haphazard way but get oriented in an orderly manner at the interface. In this connection his representation of say, palmitic acid on the surface of water has become a commonplace idea in surface chemistry. Langmuir has shown that when palmitic acid spreads on water surface, owing to the attraction of the carboxyl groups for the polar water
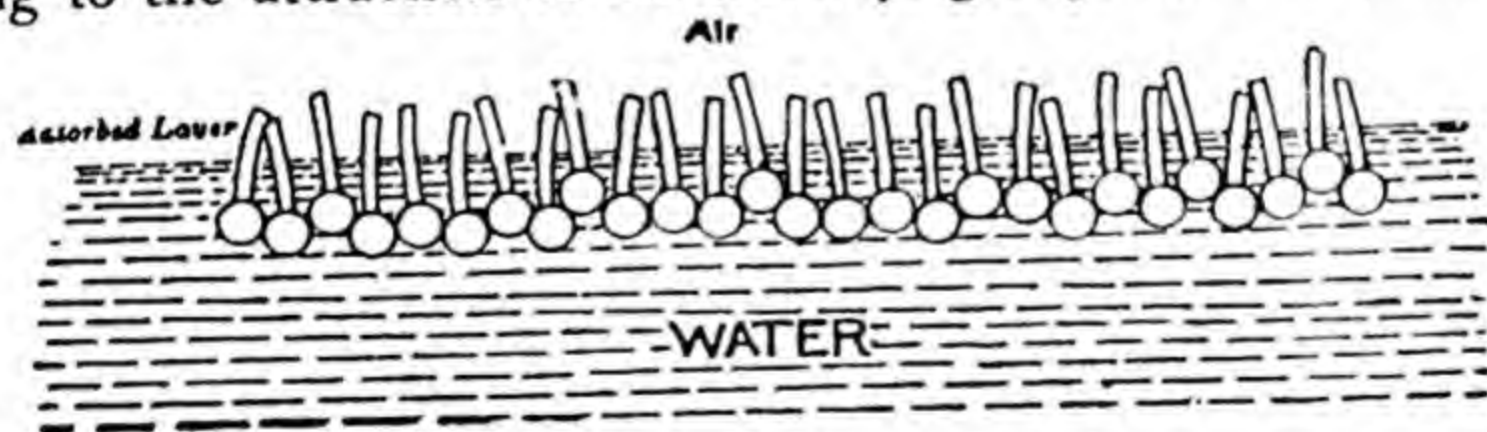

Fig. 105—Orientation at Interface

molecules, they instead of lying flat on the surface keep standing erect more or less closely packed in a mono-molecular film with their carboxyl ends downwards and the hydrocarbon ends upwards (see Fig. 105, where palmitic acid, $C_{15}H_{31}COOH$ molecule

has been represented as a rod with a knob at the end, the knob indicating the carboxyl group). In all adsorption processes, the adsorbed molecules are subject to more or less such *directional orientations* as a result of the interactions of physico-chemical forces operating at the interface.

Exchange Adsorption. Permutit.—If a salt solution say, calcium chloride is percolated through a column of clay minerals it is observed that some calcium ions are adsorbed by the clay which latter gives out an equivalent quantity of sodium ions. In the case of kaolin, the reaction can be represented as—

$$\text{Sodium kaolin} + (Ca^{++} + 2Cl^-) \longrightarrow \text{Calcium kaolin} + 2(Na + Cl^-).$$
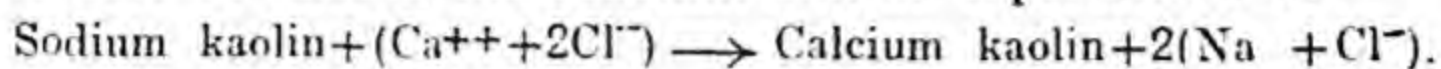
This phenomenon of adsorbing only one of the ions by a solid material in exchange for another similarly charged ion contained in the solid is called **exchange adsorption.**

Important industrial application of this is made in the softening and deionising of water. In the permutit process a very porous type of clay minerals called *zeolites* is used. Hard water is percolated through columns packed with zeolites where exchange adsorption takes place resulting in an almost complete replacement of the Ca^{++} and Mg^{++} ions by an equivalent amount of Na^+ ions from the zeolite. When the zeolite is almost exhausted of its Na^+ ions it is reactivated by percolating a solution of sodium salt through it.

De-ionisation of Water—Recently, synthetic resins similar to zeolites in properties have been developed which not only can exchange cations but can also adsorb anions and free acids. Hence, if water is percolated successively through two columns, one containing a resin which exchanges cations with its own H^+ ions and another which exchanges negative ions with OH^- ions or adsorbs acids, the percolate would be de-ionised water. In all advanced countries such deionised water which is much cheaper to produce is used in place of distilled water in many industries.

Surface-Active Agents—Soaps and various synthetic detergents, even in very small concentration, remarkably lower the surface tension of water. For example, a very dilute soap solution has often a surface tension of less than 30 dynes per cm against 72 dynes per cm, the value for pure water. Such substances which are extraordinarily powerful in depressing surface tension of water are called *surface active agents*, ordinary soaps being good examples. These are also called *capillary-active.* It can be shown theoretically that the surface active agents have a higher concentration on the surface layer where they are probably oriented as shown in Fig. 105. These compounds are of great technical importance which is briefly discussed in the section to follow.

Wetting, Emulsification, Detergency and Other Surface Phenomena— Surface-active agents as discussed in the previous section are employed though in small concentrations to perform

some highly essential functions in many industrial processes, to name a few, wetting, spreading, penetration, ore floatation, emulsification, etc. Normally a duck floats on water but if the water contains a trace of a powerful surface-active agent, the duck will get wetted and may be drowned. For similar reasons a dyeing bath must contain the right type of surface-active agents to facilitate wetting, penetration and spreading, as otherwise uneven dyeing would result. Liquid drops on say, a metal surface tend to remain as isolated drops but spread into a thin layer if a trace of good wetting agent is added. Soldering flux also serves similar purpose. The importance of wetting can be well realised from the fact that an acetone-'dry ice' mixture would freeze mercury earlier than liquid nitrogen though the latter is about 100° lower in temperature, because the former wets metals and the latter does not.

Emulsifying power, wetting, detergency, etc. are somehow connected with the surface activity though the exact mechanism is not definitely known. In fact all *phase-subdivision processes* such as emulsification, formation of spray, etc. and *phase-displacement processes* such as wetting, floatation, cleaning, etc., are intimately connected with surface activity and adsorption at an interface.

INDUSTRIAL APPLICATIONS OF ADSORPTION—Both gaseous adsorption and adsorption from solution are utilised industrially. The commercially important solid adsorbents are the following :—(a)*Fuller's earth*, (b) *Activated charcoal* of various types, (c) *Silica gel* and (d) *Activated alumina*.

Fuller's earth is used in enormous quantities for refining petroleum and vegetable oils. Activated charcoal is used for decolorising sugar solutions, for recovery of volatile solvents from air, for miscellaneous decolorising and deodorising purposes, and in gas mask. Activated alumina and silica gel are nowadays used in dehydration and purification of air and industrial gases, and the latter is used to some extent for refining petroleum distillates and also in gas mask. Among other applications are the separation of gases by fractional adsorption, vapour phase partition chromatography, corrosion protection, etc.

Exercises

1. Deduce Langmuir's adsorption equation and discuss the form this equation takes in the limiting conditions of very low and very high pressures.

2. Distinguish between Physical Adsorption and Chemisorption. Why is the latter also called activated adsorption.

3. Give a short account of surface active agents and their importance to science and industry.

4. Write notes on :—(a) De-ionised water, (b) surface orientation (c) Freundlich adsorption isotherm, (d) phase-displacement processes, and (e) exchange adsorption.

5. Can you suggest an explanation for the fact that geyser action can be set off by putting bits of soap in dormant geyser holes.

6. What peculiar phenomena you would notice if by some means the surface tension of water is tremendously increased?

CHAPTER XXIII

COLLOID CHEMISTRY

Historical Introduction—Thomas Graham in his classical researches on liquid diffusion (1861) observed that some substances could diffuse very rapidly in solution and could readily pass through animal and vegetable membranes, while there were others which failed to do so. To the former class belonged almost all inorganic acids, bases and salts and many organic compounds, *e.g.* urea, sugar, etc. Graham named them *crystalloids* since most of the members of this class could be readily obtained in the crystalline state. The other class of compounds which could not pass through the membranes was named *colloid*, from the Greek word *kolla* meaning glue, which was a typical member of this class and this process of separation of crystalloids from colloids was termed *dialysis*. The colloid class—Graham observed —comprised typical high molecular weight compounds, *e.g.* starch, gelatine, silicic acid, proteins, etc.; he ascribed their inability towards diffusion to their high molecular weights and resulting low osmotic pressures. He further supposed that the molecules being of very large size could not pass through the pores of the parchment membrane.

Colloidal State of Matter—The above view of Graham has undergone some essential modifications due to later researches. It has been shown that colloids do not form a class of substances but they are only states of matter to which all substances could be transformed with more or less ease. In a solution of NaCl in water, the ultimate units present in solution are Na^+ and Cl^- ions, but on dissolving say, sodium oleate (soap) in water, most of the ultimate units are large aggregates composed of millions of oleate ions and some undissociated sodium oleate and such solutions exhibit colloidal properties. So, in water NaCl is in true solution and sodium oleate is colloidal. However, sodium chloride can be made to remain dispersed as large aggregates in a non-solvent by some roundabout method, for example as is possible to be done in benzene, and it would be a colloidal solution of NaCl in benzene. On the other hand, sodium oleate dissolves in alcohol and can be proved to be present mainly as individual molecules of sodium oleate and not as aggregates as in water and so sodium oleate is regarded to be in true solution in alcohol. Thus, the same substance could behave as a crystalloid in one solvent and as a colloid in another.

Association Colloids and Molecular Colloids— It was observed that substances like gold, sulphur, ferric hydroxide, etc.

which are ordinarily insoluble in water, could sometimes be made to exist in apparently homogeneous solutions. These solutions also had a very slow rate of diffusion through membranes and were classed as colloidal solutions. A characteristic property of these solutions is that though they appear homogeneous to the naked eye, closer observation under a microscope or an ultra-microscope reveals the existence of *non-homogeneity* in such solutions. In fact, they are simply fine particles of matter kept in suspension in a liquid medium. From another point of view we may regard these systems as solutions in which the sub-division of the solute has not been pushed right up to the *molecular stage* but has stopped somewhere midway ; thus instead of single molecules separately existing in a true solution, here we have *a large number of stabilised aggregates of hundreds of thousands of molecules disseminated throughout a liquid medium.* This type of colloid is sometimes called *association colloids* evidently due to the formation of each colloidal particle by the aggregation of a large number of molecules. Almost all inorganic colloids such as gold sol, ferric hydroxide sol, silicic acid sol, etc. are of this type.

In contrast to the association colloids there is another class of colloids, called *molecular colloids* or *intrinsic colloids* where the molecules themselves are big enough to be of colloidal dimension and hence show colloidal properties. Proteins such as albumen, gelatin, etc., polysaccharides and their derivatives, *e.g.*, starch, cellulose and its esters, etc., and other high polymers, belong to this class as their molecular weights range from about 30,000 to well over a few millions. Some of these 'giant' molecules can form well-defined crystals owing to their high degree of symmetry. Many proteins and enzymes which though unmistakably colloidal, have also been obtained in the crystalline form. Even viruses, which in many respects seem to be on the border line between living and non-living matter, have been obtained in the crystalline state and their molecular size and weights have been measured. For example, tobacco mosaic virus, whose molecules are 300 mμ long and 15mμ in thickness and have molecular weight in the range of 50 millions, has been obtained in the crystalline state. Thus, the old idea of colloids being non-crystalline has been completely blasted by later experimental findings.

Definition of Colloids—Therefore, the essential distinction between a true solution and a colloidal solution is that in colloidal solutions the dissolved units are very much bigger than the ordinary molecules present in true solution. Hence, colloidal solutions are regarded as heterogeneous or two-phase systems in contrast with homogeneous ordinary solutions. So, we may define a *colloidal solution* as a stable two-phase (*i.e.* heterogeneous) system, one of which, usually a solid, is dispersed in a finely divided state throughout the other phase, generally a liquid. The diameters of the dispersed particles are usually between 10^{-5} to 10^{-7} cm ;

larger particles form coarse suspension, while finer particles form true solution. It will be thus seen that the essential difference between a colloidal solution and a true solution or a coarse suspension is of degree only rather than of kind and there can be no sharp line of demarcation between them.

Size of the Colloidal Particles—It will be interesting at this place to compare the size of the colloidal particles with ordinary molecules as from the following table.

Molecular diameter	Colloidal particles	Coarse suspension
10^{-8} to 10^{-7} cm.	10^{-7} to 10^{-5} cm.	10^{-5} to 10^{-3} cm.
0.1 $m\mu$ to 1 $m\mu$	1 $m\mu$ to 100 $m\mu$	> 100 $m\mu$

It is well to remember that ordinary atoms have a diameter of 2 to 5 Å (0.2 to 0.5 $m\mu$) and visible light has a wave length of 400 to 800 $m\mu$ (4000 to 8000 Å). So, the average diameter of a colloidal particle (50 $m\mu$) is about an order of ten less than the wave length of visible light and about two orders of ten bigger than that of an ordinary atom.

Perhaps the finest sol is Zsigmondy's gold sol whose particle size is about 1.6 $m\mu$ whereas the diameter of the hydrogen molecule is about $0.1 \times m\mu$. It is instructive to compare the size (diameter) of colloidal particles and other familiar small dimensions as shown below in Ångstroms (1Å $= 10^{-8}$ cm. $= 0.1$ $m\mu$).

Ordinary atoms	... 2 to 5 Å (0.2 to 0.5 $m\mu$)
Cellobiose unit in cellulose	10·3 Å (1.03 $m\mu$)
Egg albumin	4 $m\mu$
Cellulose	15 to 100 $m\mu$
Colloidal particles	... **About 2 to 100 $m\mu$**
Microscopic limit of visibility	About 250 $m\mu$
Tobacco mosaic virus	300 $m\mu$
Influenza virus	... 100 $m\mu$
Wave length of visible light	... 400 to 800 $m\mu$
Bacilli	... About 750 $m\mu$
Red Blood Cells	... About 7,500 $m\mu$

It should be emphasised that colloids have large specific surface, and all properties which we term colloidal are to be attributed to the peculiarities of the forces operating on the surface. The enormous surface of a colloid can be easily understood if we compare the surface area of 1 c.c. of a solid when it is in the form of a cube, with that of the same mass when the cube is divided into smaller cubes of side 10^{-7} cm. (1 $m\mu$) in length. In the former case, the surface area is 6 sq cm while in the latter case, the surface area is 6000 sq. meters (about one and half acres).

Dialysis—*The process of separating a crystalloid from a colloid by means of diffusion through a membrane is called* dialysis. That colloids do not pass through parchment paper or other membranes, as already stated, was first observed by Graham and this property is still the simplest criterion for ascertaining the colloidal nature of a solution and is extensively used in the purification of colloids. The apparatus used is called a *dialyser*, which in its simplest form consists of a parchment or collodion bag half immersed in water. A common form of dialyser is shown in the figure (Fig. 106). It consists of a small bell-jar, B across the bottom of which is stretched a parchment paper P and the whole is suspended in water. The mixture of a colloid and a crystalloid is put in the

Fig. 106—Dialyser

dialyser and the outside water is repeatedly changed. Meanwhile, all the crystalloids pass through the membrane into the water outside and the colloidal solution is left in the pure state. Though parchment paper has been very extensively used as membranes for dialysis in all classical colloidal investigations, sacks made of collodions or transparent cellophane (regenerated cellulose) paper are now in great favour.
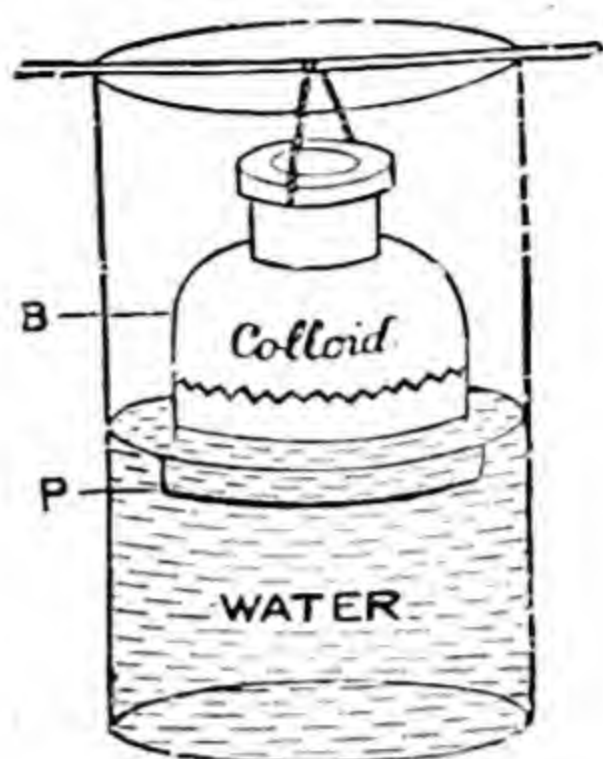
Nomenclature—It appears from the foregoing discussion that a colloidal solution is essentially a *non-homogeneous system* consisting of *two phases*, one of which, usually a solid is *dispersed* in the other one, usually a liquid. The liquid in which the dispersion has taken place is called the **dispersion medium** and the solid is called the **dispersed phase.** In colloidal gold, water is the dispersion medium and gold is the dispersed phase.

Colloidal solutions using water as the dispersion medium are called **hydrosols** or, simply, **sols.** If alcohol is the dispersion medium it is called *alcosol.* We shall call a colloidal solution of gold as simply a *gold sol.* Sols are sometimes almost as thick as a jelly, when they are called *gels.*

Classification of Colloids—Sols are frequently subdivided into two classes, (a) lyophobic (solvent-hating) and (b) lyophilic (solvent-loving) colloids. The former class includes those sols which may be regarded as simple suspensions—so sometimes called *suspensoids*—and here, there is no perceptible affinity between the dispersed phase and the dispersion medium, *e.g.* gold sol, silver sol, arsenic sulphide sol, etc. These sols are sometimes called *irreversible sols,* for, if the dispersed phase is once precipi-

tated out by some means, it is not generally easy to get it back in the colloidal state.

To the class of *lyophilic* or *reversible* colloids belong gelatine, gum-arabic, etc. all of which have a marked affinity for water. No special methods are necessary for their preparation, only the treatment of the solid with the solvent at a suitable temperature being sufficient. The colloidal particles are so highly solvated that very often such colloidal solutions are optically clear under the ultramicroscope. This type of colloids is also called *emulsoids*, and also *intrinsic colloids*.

The basic distinction between these two classes is that lyophobic sols are essentially unstable systems whereas the lyophilic sols are highly stable. Thus, typical lyophobic sols are easily coagulated by electrolytes, but not so, the lyophilic sols. It is believed that lyophilic sols are highly solvated and each particle is surrounded by a sheath of solvent molecules conferring high stability to these particles.

Distinction between a Lyophilic and a Lyophobic Colloid

Lyophobic Colloids (Suspensoids)	Lyophilic Colloids (Emulsoids)
1. Well-defined under a microscope or an ultra-microscope.	1. Invisible under a microscope.
2. Easily coagulated by electrolytes.	2. Very stable, not easily coagulated. Coagulated by adding hygroscopic substances e. g. alcohol etc. or sometimes by cooling.
3. Undergo irreversible coagulation	3. Coagulation is reversible.
4. Viscosity same as the solvent.	4. Much viscous than water.
5. Do not gelatinise readily and are very unstable on reversal of charge.	5. Gelatinise rapidly and have an iso-electric point.
6. Density, refractive index, etc. follow the law of mixtures.	6. Physical properties do not follow the law of mixtures.
7. Prepared by indirect methods.	7. Usually prepared by a simple solution process.

It should be emphasised that the distinction between the two classes is not sharp. Ferric hydroxide sol, a typical *lyophobic sol*, *is not well-defined under the microscope*, whereas silicic acid sol a *lyophilic colloid* is rather *sensitive* to small quantities of some *electrolytes*.

Preparation of Colloidal Solutions —Some organic substances, *e.g.* gelatine, starch, soaps, dyestuffs, etc. form colloidal solutions by being simply dissolved in water. In some cases, *e.g.* mastic, gamboge, palmitic acid, etc., alcoholic solutions of the substances are poured in warm or boiling water and the alcohol is removed by gentle warming to get a colloidal solution.

For inorganic colloids, special methods are usually necessary which may be broadly divided into two heads ;—(*i*) *Condensation method i.e.* a method in which particles of colloidal size grow up

by the agglomeration of substances dispersed in the molecular state ; and (ii) *the disintegration method*, in which the substance in bulk is broken down into particles of colloidal size. The preparations of some typical colloids are described below.

(a) ARSENIOUS SULPHIDE SOL—Through a saturated aqueous solution of arsenius oxide is passed a slow stream of sulphuretted hydrogen. The arsenious sulphide formed remains in the colloidal state giving the whole solution a transparent yellow colour. The dissolved H_2S is expelled by bubbling hydrogen through the warm sol. The sol, thus obtained, is very pure and is suitable for class-room demonstration of coagulation and other properties of colloids.

(b) FERRIC HYDROXIDE SOL—To vigorously boiling distilled water, is added, drop by drop, a freshly prepared staturated solution of ferric chloride. As each drop falls in the water it suffers hydrolysis ($FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl$). forming a deep red sol. The sol obtained is rapidly dialysed in a parchment bag against warm water to free it from the HCl and undecomposed $FeCl_3$.

(c) SILICIC ACID SOL AND GEL—To a solution of sodium silicate, commercially known as water glass or soluble glass, made to a sp. gr.—1·14 is run in a solution (4N) of HCl with constant stirring until the acid is in excess. The mixture is diluted to more than twice its volume and dialysed for a few days against running water, until the dialysate is free from HCl.

To prepare silica gel all that is required is to use a more concentrated solution of the silicate and to allow the dialysis to continue for a longer time when the sol ultimately sets to a jelly. If a strong solution of sodium silicate is acidified with acetic acid or any acid, and set aside, the whole thing sets to a transparent jelly.

(d) COLLOIDAL SULPHUR (*Oden's method*)—A strong solution of sodium thiosulphate (3N) is added drop by drop to conc. sulphuric acid. The solution on cooling deposits sulphur, which is washed with water. This mass of sulphur dissolves completely in water to give a clear colloidal solution which may be purified by dialysis or by re-precipitating with sodium chloride, washing and redispersing in water.

(e) ZSIGMONDY'S GOLD SOL—This is prepared by the reduction of gold chloride with formaldehyde, glucose, hydrazine, etc. To 120 c.c. of redistilled water containing 15 mg. of gold hydrochloride ($HAuCl_4 \cdot 3H_2O$) and 37 mg. of pure K_2CO_3, is added 0·5 c.c. of a dilute ethereal solution of phosphorus. A bright red sol results. On adding electrolytes the red colour changes to blue owing to an increase in the size of the colloidal particles.

(f) COLLOIDAL METALS : BREDIG'S METHOD—Bredig's method of preparation of colloidal metals consists of establishing a direct-current arc between two wires of the same metal used as electrodes,

the ends of the metal being kept immersed under water in a well-cooled vessel. On the passage of current the ends of the metals are torn off and fine particles of metal remain suspended in the liquid medium. Sols of gold, silver, platinum, etc., can be prepared in this way.

PROPERTIES OF COLLOIDAL SOLUTIONS

General Properties. **(a) Colour**—The colour of a colloidal solution is not always the same as the colour of the substance in bulk. Gold sol prepared by Zsigmondy's method is red in colour or is a mixture of *red and blue* depending on the size of the colloidal particles. Sulphur sols may be colourless, faint yellow or deep yellow in reflected light and reddish in transmitted light and it has been possible in some cases to calculate the particle size from the colour of the sol. Some sols notably of vanadium pentoxide, palmitic acid, etc. assume a beautiful *silky appearance* when the sol is stirred, and the phenomenon has been traced to the *asymmetric* (rod or disk-like) shape of the colloidal particles.

(b) Density—The density of lyphobic sols can be calculated from the density of the dispersed phase and the dispersion medium, since it usually follows the law of mixtures. But the density of lyophilic colloids, such as gelatine, glue, etc. can not be calculated simply by the law of mixtures, since, during their formation there is usually a contraction in volume. For example, a colloidal solution containing 10 gms of gelatine in 100 cc. of water occupies only a volume of 96.07 c.c.

(c) Osmotic Pressure and Molecular Weight—The osmotic pressures of colloidal solutions are very small and the experimental determination for *lyophobic colloids* is not possible due to the difficulties encountered to completely free this type of colloidal solutions from the last traces of electrolytes. The presence of a trace of electrolyte so much modifies the value of the osmotic pressure that the effect due to the colloid may even remain completely masked. The osmotic pressures of some *lyophilic colloids* particularly molecular colloids, *e.g.* proteins, cellulose and its derivatives, rubbers, high polymers, viruses, etc. have been determined with some degree of certainty. In fact, this is one of the best methods of obtaining reliable values of the molecular weights of such colloids (*vide* P. 182).

Optical Properties. **(a) Tyndall Phenomenon**—If a streak of sunray is passed through a dark room, the dust particles in the path of the light become clearly visible, due to the scattering of light from their surface. Since lyophobic colloids are essentially heterogeneous systems, the same principle may be applied to observe the colloidal particles. If a colloidal solution whose particle size is so small as not to be detectable under a microscope (below about 0.2μ) is placed under the instrument against a dark background and a strong beam of light is passed at right

angles to the line of view, the field becomes at once filled with coloured specks of light due to the scattered light from the colloidal particles. The individual particles, which were otherwise invisible, could be thus observed and counted. The above phenomenon is known as Tyndall effect and the apparatus for viewing the colloidal particles, utilising the above principle, is called *ultramicroscope* (Fig. 107), first constructed and used by

Fig. 107—Principle of ultra-microscope.

Zsigmondy (1902). Its limit of resolution is about 6mμ i.e. 60Å.

(b) Brownian Movement—In the year 1827, the English botanist Robert Brown observed that pollen grains dispersed in water executed a ceaseless random motion. The cause of this motion was first suspected to be mechanical vibration or convection current. But painstaking researches have shown that this motion persists even when confined for years in underground cellars. It has been found that this random zigzag motion is executed by all colloidal particles, including colloidal particles suspended in a gaseous medium, independent of their nature,
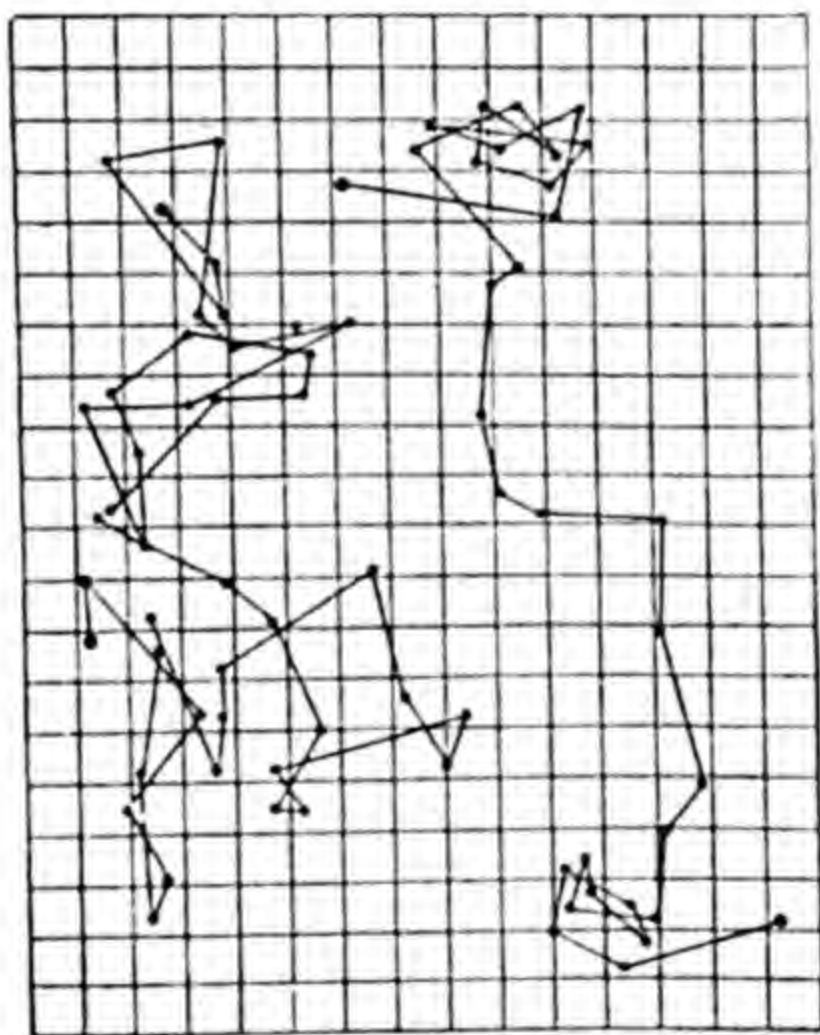
Fig. 108—Brownian motion

smaller particles executing a more rapid and brisk motion than the larger ones. This ceaseless zigzag motion of the colloidal particles is called *Brownian movement* after the name of the discoverer. This completely erratic, zigzag movement is described by Perrin as "they go and come, stop, start again, mount, descent, remount again, without in the least tending towards

immobility." Fig. 108 is a graphical representation of the Brownian motion of two colloidal particles, the position of each particle being continuously located by a microscope after a constant small interval of time.

The true cause of the phenomenon was first suggested by Wiener (1863), as being due to the unbalanced impacts of the liquid molecules on the colloidal particle. The colloidal units are constantly hit from all sides by the surrounding solvent molecules and are tossed up just like a ship in a stormy sea. In fact the Brownian movement is a direct demonstration of the ceaseless motion of molecules pictured by the kinetic theory.

A simple calculation shows this to be true. Colloidal particles are roughly 10^3 times larger in diameter than, say, an oxygen molecule and therefore have a mass about 10^9 times (cube of 10^3). Therefore, if such a colloidal particle has the same kinetic energy as a gas molecule its speed would be $1/\sqrt{10^9}$ times. Now, an oxygen molecule has a speed of the order of 5×10^4 cm. per sec. (P. 15) and so a colloidal particle of average size would have speed of the order of $5 \times 10^4/\sqrt{10^9}$ i.e. a few cm per sec., which is just quite suitable for visual observation as a brisk motion.

Electrical Properties. (a) Electric Charge of Colloids and Cataphoresis —If the lower part of a U-tube is filled with a colloidal solution and the rest filled with distilled water and a potential gradient is applied along the tube by means of two platinum electrodes, the colloid moves either towards the cathode or towards the anode with a speed of the order of 10^{-5} cm. per sec. per unit potential gradient (about ten times slower than ordinary ions). So, it is found that colloidal particles are charged like ions. This phenomenon of movement of a colloid in an electrical field is known as **Cataphoresis** or by the wider term *electrophoresis*. The colloids may be positively or negatively charged as shown in the table. This charge, most likely, is due either to adsorption of ions by the colloidal particles or to ionisation of ionisable or dissociable groups present on the surface of colloidal particles.

Positively charged	*Negatively charged*
The hydroxides, e.g. Fe(OH)$_3$, Al(OH)$_3$, Cr(OH)$_3$ etc.	The sulphides, e.g. AS_2S_3, etc. The metals, e.g. Au, Pt, etc. Silicic acid, vanadium pentoxide Organic colloids, e.g. starch, gum arabic, etc.,
Basic dyes	Acid dyes.

Lyophilic colloids like albumen, gelatine, etc. are positively charged in strongly acid solution and negatively charged in alkaline solution ; for any colloid of this type there is a concentration of hydrogen ion at which it moves neither to the cathode

nor to the anode. This concentration of H^+ ion (or, pH) is called the **isoelectric point** of the colloid, and usually covers a small range of pH. The isoelectric point of hemoglobin from various sources lies in the pH range 4.3 to 5.3 and that of gelatin round pH 4.7.

COLLOIDAL ELECTROLYTES—If a soap (say, Na-palmitate) is dissolved in water it dissociates into Na^+ and palmitate ions. But the palmitate ions, due to their strong cohesion, form groups of such ions which may become of colloidal dimension. Such aggregates of ions which of course, may contain a few undissociated molecules are called *micelles* and the colloidal properties of soap solutions are due to the presence of these micelles. The micelles are however, good conductors of electricity due to their ionic nature. Soap solutions are therefore fairly strong electrolytes with colloidal properties and so, are called *colloidal electrolytes*.

(b) Coagulation of Lyophobic Colloids—If a small amount of an electrolyte is added to a lyophobic colloidal solution, it is observed that the sol gradually gets turbid and ultimately the dispersed phase separates out as a flaky precipitate. This phenomenon is called *coagulation* or precipitation of a colloid, and the solid which separates out under such conditions is called the *coagulum*. As observed under the microscope or ultramicroscope, coagulation consists simply of the aggregation of the smaller particles into larger ones, which are big enough to settle down.

Ferric Hydroxide sol.		Arsenious Sulphide sol.	
Electrolyte	Coagulating concentration *milli mols per litre*	Electrolyte	Coagulating concentration *milli mols per litre*
NaCl ...	9·25	NaCl ...	51
$\frac{1}{2}BaCl_2$ ...	9·64	KNO_3 ...	50
KNO_3 ...	11·9	$\frac{1}{2}K_2SO_4$ ...	65·5
K_2SO_4 ...	0·204	$MgCl_2$ ...	0·72
$MgSO_4$ ...	0·217	$MgSO_4$ ...	0·81
		$BaCl_2$ ...	0·69
		$AlCl_3$ ...	0·093
		$Al(NO_3)_3$ ...	0·095
		$\frac{1}{2}Al_2(SO_4)_3$ ...	0·096

The coagulating power of different electrolytes is not the same. It is almost solely determined by the valency, *i.e.*, the electric charge of the ion having a charge opposite to that of the colloid. It may be observed from the table that for coagulating the positively charged ferric hydroxide sol the divalent sulphate ions are about 50 times more powerful than the monovalent

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chloride or nitrate ions, and similarly also for the negatively charged arsenious sulphide sol a higher positive valency is a more effective coagulant. This fact was observed by various workers and is referred to as the **coagulation rule** which may be stated thus—*the coagulating power of an electrolyte depends only on the valency of the ion bearing a charge opposite to that of the colloidal particle.*

Perhaps, the mechanism of coagulation is a neutralisation of the charge of the colloids by the oppositely charged ions of the added electrolyte, and subsequent agglomeration of the particles. This seems more plausible from the experimentally observed fact that by mixing up two colloidal solutions, which are oppositely charged, both of them get coagulated. This is known as *'mutual coagulation of colloids'.*

(c) Protective Action of Lyophilic Colloids—Lyophilic colloids are not only themselves highly stable but when added to a lyophobic sol impart stability to the latter, making the latter much less sensitive to coagulation by electrolytes. In extreme cases such stabilisation makes it possible for the stabilised colloid to be dried and redispersed.

The protective power of hydrophilic colloids differs widely among themselves, and this is made the basis of a quantitative determination of protective power by gold number. **Gold number** is defined as *the number of milligrams of the hydrophilic colloid which just fail to prevent a change in colour (red to violet) of a standard gold sol by the addition of 10 c.c. of ten per cent sodium chloride solution.* Some representative data are given in the table, where it would be observed that the protein gelatin has a much lower gold number (*i.e.* higher protective action) than the nonproteins. Gold number has diagnostic value in medicine because in some diseases of the nervous system the cerebrospinal fluid shows characteristic change in its gold number.

Substance	Gold number
Dextrin	125 – 150
Starch	10 – 15
Gum Arabic	0·10 – 0·15
Gelatin	0·005 – 0·0125

(d) Peptisation—If a colloidal solution is coagulated, the coagulum will not usually pass into the colloidal state again. But, sometimes, it happens that by simply washing down a precipitate or by adding a dilute solution of a suitable electrotyle, the coagulum again passes into the colloidal state. Fresh coagulum of ferric hydroxide easily passes into colloidal solution when treated with dilute ferric chloride solution ; the latter may be then removed by dialysis to produce a stable sol. *This process of transferring back a precipitate or coagulum into colloidal form is called peptisation.*

ULTRAFILTRATION—A colloidal solution easily passes through an ordinary filter paper, since, its pores are not small enough to retain the colloidal particles. Bechhold, however showed that a properly supported membrane of collodion or hardened gelatine could retain the colloidal particles. He prepared membranes of different pore size by varying the concentration of the collodion. By using a series of such membranes it becomes easy to determine the particle size of a colloid, by observing whether a given membrane allows the colloid to pass through or not. Such a series of collodion filters of different pore-sizes are known as *graded filters* and the process of filtration of colloid through such membranes is called *ultrafiltration*.

Emulsions—If the dispersed phase is a liquid, the colloid thus formed, is known as an emulsion. So, we may define an emulsion as *a system containing two liquid phases one of which is dispersed as globules in another*. The most common example of emulsion is milk, which is simply fine particles of fat suspended in an aqueous medium ; this type of emulsion is known as *oil-in-water* type. Butter on the contrary, is an emulsion of the opposite type (*water-in-oil*), where fine particles of water are disseminated in a medium of fat.
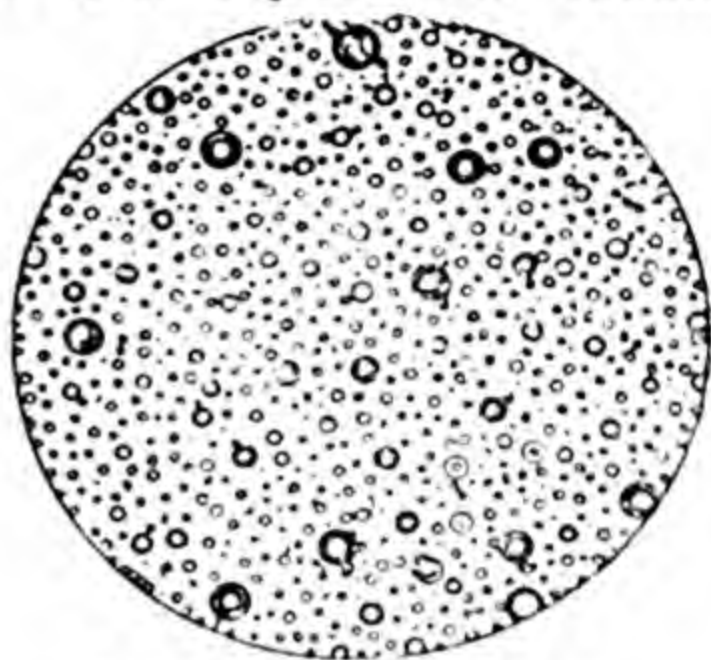
Fig. 109—Milk as seen under a microscope

The shaking of an oil with water does not necessarily make an emulsion for, the oil and water soon separate into two layers when allowed to settle. It is necessary for the stability of an emulsion to add an *emulsifier* or *stabiliser*. The alkali metal soaps, gum acacia, gum tragacanth, etc., are good stabiliser for emulsions of the oil-in-water type, whereas heavy metal soaps are emulsifiers of the opposite type. The pharmaceutical emulsions, such as cod-liver oil emulsion, Angier's emulsion, etc., are of the oil-in-water type, in which various substances, *e.g.* egg-yolk, casein, gums, Irish-moss, saponin, etc., have been added as emulsifiers.

Gels—Sols of gelatine and agar on cooling set to a coherent jelly-like mass, and to this is applied the term gel. In spite of the percentage of the dispersed phase being very small, the gels produced possess some of the properties of solids. A less than 2 per cent agar solution when cooled sets to a rather stiff gel. So, by the term gel may be understood "*transparent or opalescent masses containing a large percentage of liquid which retain their shape, offer some resistance to mechanical deformation and show no microscopic structure*".

Gels are generally divided into 'elastic' and 'rigid' gels. Gelatine, agar, etc. belong to the former class, while silicic acid gel and most inorganic precipitates fall under the latter category.

The pure gel, if left in air, rapidly loses water, even at ordinary temperature, and dries to a glass-like transparent mass. For some dilute gels, the dispersed phase shrinks on standing with the consequent separation of some of the liquid dispersion medium and this is called '*syneresis*'.

The structure of the gels is still a matter of controversy but it is usually assumed that it is *two-phase fibrillar or network structure* of the solid phase, dispersed in a liquid phase. It should however, be pointed out that the term *gel* itself is indefinite and applies to a variety of substances, which may not have a common structure.

Importance of the Study of Colloids —An understanding of the behaviour of matter in this finely divided state has both theoretical and practical possibilities. But the greatest fascination that this borderline science holds out is certainly the fact that life itself, the whole protoplasmic structure and its reactions, is colloidal—a fact very tersely expressed by Fischer by saying that *"Colloid chemistry is the twilight, between chemistry and physics—but that is where God has chosen to reveal Himself."*

Many commercial processes involve the use of colloidal substances but here, as in many cases, the art has far outrun the science and most industrial knowledge has been developed on an empirical basis. In large *industries* such as *tanning, dyeing,* manufacture of *paints, photographic plates, lubricating grease, etc.,* the substances treated are more or less of a colloidal nature and a knowledge of this science is essential for the proper controlling of the processes. Many *pharmaceutical preparations* are either emulsions, or colloidal suspensions, for, matter in this finely divided state is supposed to be very active and easily assimilated by the various organs of the body, though "there is no evidence that the therapeutic effect of drugs in the colloidal state is better than that of the same drug in the crystalloid state" (Quoted from Hale-White's Materia Medica).

Exercises

1. What is Graham's definition of a colloid? In what important respect his ideas have been modified?

2. Write short notes on :—(a) Dialysis (b) Ultramicroscope (c) Peptisation (d) Cataphoresis (e) Permutit (f) Tyndall phenomenon. (g) Brownian movement, (h) Iso electric point and (i) lyophilic and lyophobic colloids, and their stability towards coagulants.

7. What is dialysis? Describe what happens when the following are dialysed :—(a) milk, (b) blood plasma, (c) supernatant liquid of boiled rice and (d) acidified solution of sodium silicate.

PART VI

STRUCTURE OF MATTER

Atomic Theory in the Pre-electron Era—Elementary
Particles: Radioactivity—Nuclear Theory of the Atom
—Electronic Theory of Valency.

CHAPTER XXIV

ATOMIC THEORY IN THE PRE-ELECTRON ERA

Dalton's Atomic Theory —Towards the beginning of the last century (1808) John Dalton propounded his celebrated atomic theory, according to which substances are composed of an immense number of exceedingly small particles which are themselves indivisible by any chemical process. These small particles are called atoms, and chemical union is merely a juxtaposition of atoms.

The vast mass of chemical facts including the law of conservation of matter and the laws of stoichiometry, *viz.* laws of constant, reciprocal and multiple proportions, and similar other hitherto observed regularities, received an able explanation in the light of this theory.

The atomic concept of matter was no new idea; it was freely used in the writings of earlier Greek and Indian philosophers. Boyle (1661), Newton (1730), and others, also tacitly assumed the atomic nature of matter and two Irish chemists, Higgins (1789) by name, got so close as to suggest that chemical combinations were really union between atoms but made the wrong assumption that the atoms of all substances were equal in weight.

Atomic Weights—Just after the publication of atomic theory, there followed a busy period in which chemists were engaged in determining the relative atomic weights of the different elements the weight of the hydrogen atom being taken as standard which was later changed to the oxygen atom $(O = 16)$ for practical reasons. As there was no rational method of knowing the chemical formula of a compound, much confusion arose and different systems were in use and the whole situation was in a hopeless confusion until Avogadro clarified the distinction between atoms and molecules and propounded his celebrated hypothesis. The situation however continued to remain somewhat confused until in as late as 1858 Cannizzaro pointed out how the Avogadro's hypothesis might be utilised for the determination of atomic weights on an unambiguous basis. It became then possible to draw up atomic weight tables on sound theoretical basis which was unanimously admitted and extensively used by chemists in general.

Determination of Atomic Weights by Chemical Methods —The basis of all chemical methods of atomic weight determinations is exact analysis by which we can accurately know the equivalent weight of different elements, *i.e.*, the weight of an element which combines with or displaces from a compound 8 parts by weight of oxygen or the equivalent weight of any other

element. The latter is related to its atomic weight by the simple relation:—

Equivalent weight × Valency = Atomic weight

or in other words, the atomic weight is an exact multiple of the equivalent weight.

So all chemical methods of determination of atomic weights involve either directly or indirectly two steps, (1) the determination of equivalent weight and (2) the determination of valency *i.e.*, an integer multiplier, the product of which and the equivalent weight gives the atomic weight. The equivalent weight is accurately determined by an analysis of any simple compound of an element, for details of which the student is referred to any text-book of inorganic chemistry. An approximate knowledge of the atomic weight added to the knowledge of equivalent weight serves the same purpose as the determination of valency. The true atomic weight is then obtained by multiplying the equivalent weight by a suitable whole number which brings the value closest to this approximate value. During the historic period of atomic weight determination, the following methods were taken recourse to, to arrive at accurate or approximate atomic weight values.

(a) Volumetric Method of Avogadro
(b) Law of Dulong and Petit (1819).
(c) Law of Isomorphism of Mitscherlich (1820).
(d) Periodic Table (1869).

It may be pointed out that the equivalent weight is a constant more fundamental than the atomic weight, as it is directly determined from experimental data and is, therefore, independent of any hypothesis. On the other hand, atomic weights are values which are based on a theory on the ultimate constitution of matter. Hence, atomic weight may lose its significance if our atomic conception changes but the values of equivalent weights will retain their importance for all times to come.

(a) Volumetric Method of Avogadro—This method utilises Avogadro's hypothesis for determination of molecular weight of the element, if gaseous, or of its gaseous compounds, from density measurements. From such molecular weight values it is an easy step to determine the atomic weight.

(b) Dulong and Petit's Law—Another method for the determination of a rough value of the atomic weight is the approximate relation discovered by Dulong and Petit. For solid elements, Dulong and Petit state that

Specific heat × Atomic weight = 6·4 (approx.)

It is a really striking fact that though the atomic weight values range from 7 (lithium) to 238 (uranium), their products with their respective specific heats always come down to a value as low as 6 (*vide* Ch VI).

From the above relation, the atomic weight of any solid element is approximately known from a measurement of its specific heat. The equivalent weight is accurately determined experimentally and is multiplied by some integer (valency) which gives a value closest to the approximate value thus determined by the Dulong and Petit's law. An example is shown below:—

EXAMPLE 1. *The oxide of a metal contains 21·42 per cent oxygen. The specific heat of the metal is 0·109. Find the atomic weight of the metal.*

$$\text{Equivalent weight} = \frac{\text{wt. of oxygen}}{\text{wt. of metal}} \times 8 = \frac{78·58}{21·42} \times 8 = 29·34$$

$$\text{From Dulong and Petit's Law, Approx. at. wt.} = \frac{6·4}{\text{sp. heat}} = 58·77$$

$$\therefore \quad \text{Valency} = \frac{\text{approx. at. wt.}}{\text{eq. wt.}} = \frac{58·77}{29·34} = 2 \text{ (since valency is a whole}$$

number). ∴ True atomic weight = eq. wt. × valency = 29·34 × 2 = 58·68.

For further discussion on Dulong and Petit's Law consult the chapter on the properties of solids (Ch. VI).

(c) **Mitscherlich's Law of Isomorphism**—Mitscherlich observed that substances, specially the phosphates and arsenates which have similar structure crystallise in the same crystalline form with equal number of molecules of water of crystallisation. These salts could also form mixed crystals or overgrowth and were called by him isomorphous. From these and similar observations he put forward his well-known law of isomorphism, which may be stated in the following way :—*Compounds which have identity of crystalline form (i.e. isomorphous) have similarly of structure i.e., an equal number of atoms connected in the same way.*

For a more detailed discussion of the law, the chapter on solids may be consulted (Ch. VI).

If one element replaces another in a compound without changing the crystalline form, the law of isomorphism asserts that the element has been replaced atom for atom. Therefore, *the replacing quantities of these two elements are to one another as the ratio of their atomic weighs* and so, if one of the elements be of known atomic weight, the atomic weight of the other can be calculated.

Aluminium oxide, ferric oxide and chromic oxide are isomorphous since the above minerals have the same crystalline form and are also found together as mixed crystals. If the atomic weight of any one of these elements is known, the atomic weights of the other two can be easily calculated from an analysis of their oxides.

N. B. The student should note that if two elements A and B form two isomorphous compounds, the percentage of A : percentage of B is not

equal to the ratio of their atomic weights; the latter ratio is only equal to the ratio of the replacing quantities of A and B, *i.e.* the weight of A in a molecule : the weight of B in a molecule.

EXAMPLE 2. *Potassium selenate is isomorphous with potassium sulphate and contains 35·77 per cent. selenium. Calculate the atomic weight of selenium.*

Potassium selenate is isomorphous with potassium sulphate (K_2SO_4) and so has got the formula K_2SeO_4.

Molecular weight of potassium selenate $= 2 \times K + Se + 4 \times 0$
$$= 2 \times 39·095 + Se + 4 \times 16 = 142·19 + Se$$

Therefore, the percentage of selenium $= \dfrac{Se}{142·19 + Se} \times 100 = 35·77$

$$\therefore \ \frac{Se}{142·19 + Se} \times 100 = 35·77 \quad \therefore \ Se = \frac{35·77 \times 142·2}{64·23} = 79·16$$

Hence, the atomic weight of selenium is 79·16.

Since this method depends upon accurate chemical analysis, the atomic weight values obtained are sufficiently accurate and need no further correction by comparison with equivalent weights. Also, even if the molecular formula of none of the isomorphous compounds is known, the atomic weight can still be found out from the law of isomorphism, as will be explained by an example (see Example (5) at the end of this chapter.)

(*d*) **Periodic Table** —The periodic table (for a brief discussion, see Ch. XXVI) may sometimes give a clue to the approximate value of the atomic weight. For example, indium was found by analysis of its oxide to have an equivalent weight equal to 37·9; so its atomic weight should be an exact multiple of 37·9. Mendeleeff pointed out that in consideration of its similarity of properties with the third group elements, it was to be placed in Gr. III of the table and the available vacant space in group III was between cadmium (atomic weight—112) and tin (atomic weight—118). So, the atomic weight of indium should lie between these two values. Therefore the true atomic weight should be 37·9 × 3 = 113·7 and not 75·8 (37·9 × 2) which was the then accepted value. The atomic weight of beryllium was also corrected from similar considerations.

Determination of Atomic Weight by Physical Methods.
(*e*) **Mass Spectrographic Method**—Physicists have developed a method of accurately determining the weights of atoms contained in a sample with the help of an apparatus called mass spectrograph. A rather crude apparatus was originally devised by Thomson which has been later developed into a precision instrument by Aston in England and Dempster in U. S. A. The present-day apparatus has an accuracy of about one part in 100,000 and requires a very small quantity of the substance, say, a milligram or so. With the recent spectacular growth of nuclear

chemistry and the use of isotopes as 'tracers' in various fields of science, this apparatus is finding increasing use day by day.

The principle of the method is rather simple. The substance under electric discharge of very high voltage and under high vacuum forms gaseous positive ions which move towards the cathode and fly past the cathode if the latter is perforated These ions which are charged atoms or groups of atoms are passed through electric and magnetic fields in such a way that all ions of the same charge: mass ratio (e/m), irrespective of their velocity, are focussed on one line on a photographic strip, P placed to receive them (Fig. 110). From the position and intensity of the

Fig. 110—Mass Spectograph (Schematic)

blackened line on the photographic strip or by using suitable electric detectors in place of the photostrip, the atomic weight and the relative abundance of the corresponding atomic species in the original sample are calculated. The method is so precise that the oxygen isotope ^{17}O (atomic mass 17·0045) can be distinguished from the OH^+ ion (17·008), or doubly charged helium can be distinguished from singly charged heavy hydrogen. Fig. 111 shows schematically the mass spectia of argon.

Fig. 111—Mass spectra of Argon and Krypton

(b) *X-ray Method*—By the use of X-rays it is possible to determine the volume of the smallest unit whose continuation in space builds the actual crystal. This smallest unit of the crystal also called unit crystal lattice (P. 67) usually contains a small number, say one, two, four, etc., of atoms or molecules. From density data we can calculate the weight of the unit lattice which divided by the actual number of atoms in unit lattice of an element gives the absolute weight of the atom from which atomic weight on the O = 16 scale can be easily calculated.

Chemists' and Physicists' Scale of Atomic Weights —In the earlier period when nothing was known about the structure of atoms, chemists quite logically chose O = 16 *i.e.* ordinary oxygen = 16 as their standard. Physicists however demonstrated with the help of mass spectrograph that ordinary oxygen is not entirely homogeneous but is composed of three types of atoms, the three isotopes of oxygen, O^{16}, O^{17} and O^{18}, the heavier two being present in very small quantities (P. 392). Since atomic weights of all individual atoms are very near to whole numbers and the

nuclear physicists are concerned only with the separate isotopes. the physicists have quite reasonably chosen the most abundant isotope in ordinary oxygen as their standard and have assigned $O^{16} = 16$ and they reckon the atomic weights of all atoms against this standard. It should be noted that the chemical method gives the average atomic weight of any sample whereas physicists are generally concerned with the atomic weight of each isotope separately, and the relationship is

1 unit (Chemical Scale)= 1·000272 units (Physical Scale).

EXAMPLE 3.   *An element, A forms a volatile chloride of vapour density 133. The equivalent weight of the element is 40·082. Find the atomic weight of the element.*

Let the valency of A be x and so the formula of the chloride is AClx

∴   Molecular weight of AClx = atomic weight of A+x×at. wt. of chlorine ; or 2×vapour density=equivalent weight of A×valency+x ×atomic weight of chlorine.

or $2 \times 113 = (40·08 \times x) + (x \times 35·5)$

or $x=3$ (to nearest whole number)

∴   Atomic weight of A$= 3 \times 40·082 = 120·246$.

EXAMPLE 4.   *The chloride of a newly discovered element (rhenium) contains 27·57 per cent chlorine and its position in the periodic table is between tungsten (184·0) and osmium (191·5). Calculate its atomic weight.*

$$\text{Equiv. wt} = \frac{\text{wt. of Rhenium}}{\text{wt. of Chlorine}} \times \text{Eq. wt. of Chlorine} = \frac{100 - 27·57}{27·57}$$
$\times 35·45 = 93·16$.

∴   Atomic wt. $= 93·16 \times 2 = 186·32$ for, by multiplying the equiv. wt. by the whole number 2. the atomic wt. comes in the desired range.

EXAMPLE 5.   *A complex silicofluoride is isomorphous with a similar stannifluoride, the molecular formula of both being unknown. A partial analysis of the former gives 51·76 per cent of fluorine and 12·75 per cent of silicon, while the stannifluoride contains 38·19 per cent of tin and 36·67 per cent of fluorine. Calculate the atomic weight of tin, given that of silicon is 28·06.*

In the silicofluoride 51·76 gms. of fluorine combine with 12·75 gms. of silicon ∴ 1 gm. of fluorine combines with 12·75÷51·76 gms of silicon. In the stannifluoride 36·67 gms. of fluorine combine with 38·19 gms of tin.

∴   1 gm. of fluorine combines with 38·19÷36·67 gms of tin.

∴   According to Mitscherlich's Law.

$$\frac{\text{wt. of silicon combining with 1 gm. of fluorine}}{\text{wt. of tin combining with 1 gm. of fluorine}} = \frac{\text{at. wt. of tin}}{\text{at. wt. of silicon}}$$

∴   at. wt. of tin $= \dfrac{38·19 \times 51·76}{36·67 \times 12·75} \times 28·06 = 118·6$

EXAMPLE 6.   *Richards (1914) gives the following data :—(a) 100 gms. of lithium perchlorate yield on reduction 39·845 gms. of lithium chloride, (b) one gm. of the chloride requires 2·5446 gms. of silver for complete precipitation as silver chloride and (c) one gram silver forms 1·3287 gms. of silver chloride. Find the atomic weight of lithium, silver and chlorine, assuming the formulae of all the compounds.*

From (a) $LiClO_4$: $LiCl = 100 : 39·845$.

i.e. $(LiCl + 4 \times 16)$: $LiCl = 100 : 39·845$ ∴ $LiCl = 42·393$

Now, from (b) $LiCl$: $Ag = 1 : 2·5446$

or, $42·939$: $Ag = 1 : 2·5446$ ∴ $Ag = 107·871$

From (c) $Ag : AgCl = 1 : 1·3287$

or, $107·871$: $(107·871 + Cl) + 1 : 1·3287$ ∴ $Cl = 35·454$

∴ $Li = LiCl - Cl = 42·393 - 35·454 = 6·939$

With regard to the method illustrated in the above example (Ex. 6) the student should very clearly appreciate that this is simply the fundamental method of atomic weight determination (i.e. at. wt. = eq. wt. × valency) just presented in a somewhat disguised form. For, the analytical data serve the same purpose as the determination of equivalent weights or combining ratios and the assumption of the chemical formulae of all the compounds is exactly equivalent to a knowledge of the valencies. In fact, as stressed earlier, all chemical methods of atomic weight determination reveal themselves by ultimate analysis to consist of these two steps either explicitly or implicitly.

Exercises

1. Discuss the methods of determining atomic weights. Which of them in your opinion is most suitable for chlorine, iron, nitrogen and carbon respectively.

2. What do you know of Dulong and Petit's Law and discuss its merit as a method for the determination of atomic weights of elements.

3. State Mitscherlich's law of isomorphism and point out its importance in atomic weight determination. Is it necessary to know the formulae of the isomorphous compounds in the determination of atomic weight by this method ?

4. Two elements A and B form two similar isomorphous compounds in which the percentages of A and B are x and y respectively. Criticise and correct the statement, $x : y =$ atomic wt. of A : atomic wt. of B.

5. Suppose you are given two samples of water, ordinary water and heavy water (D_2O) respectively. Propose a method by which it is possible to prove conclusively that the heavy hydrogen (D) present in heavy water has twice the atomic weight of ordinary hydrogen.

6. In a planet outside the earth all elements are the same as on earth except chlorine which is composed of only one isotope viz. Cl^{35}. Had Stas chosen to carry out his classical determination of atomic weight of silver (i.e. determination of silver : silver chloride ratio) by importing all chemicals from this planet without any knowledge of the above fact, would he have obtained the same value as he had actually obtained ? Discuss quantitatively the percentage difference, if any.

7. Will the atomic weight table expressed in the same scale as that of ours, used by the inhabitants of the planet referred to in exercise (6) be in any way different from our table ?

8. Suppose by some catastrophe all oxygen (free and combined) atoms present in this earth are annihilated except O^{16} which remains, will it be possible for the people surviving this catastrophe to use the same atomic weight table as we are using now ?

9. An analyst is using a balance but he does not know that his balance is defective and always gives exactly two per cent high value. Suppose he carries out an atomic weight determination by weighing out

silver and silver chloride obtained from it. Discuss to what extent his determined atomic weight value of silver would be in error.

10. Iron oxide contains 69·956 per cent iron, whose specific heat is 0·115. Calculate the atomic weight of iron. [55·88]

11. The vapour density of a metallic bromide is 268 (H=1) and it contains 89·85 per cent of bromine. Specific heat of the metal is 0·225. Find the atomic weight of the metal and the molecular formula of the bromide. (Br.=80). [28·2, $M_2 Br_6$ [

12. The bromine in 1·9171 gms. of hafnium bromide is equivalent to 2·9298 gms. of silver bromide. The atomic weight of silver and bromine are 107·88 and 79·916 respectively. If the specific heat of hafnium is approx. 0·037, deduce the atomic weight of hafnium and the formula of the bromide. [171·6; Hf Br_4]

[Hint :—wt. of Hf : wt. of ArBr : eq. wt. of hafnium : eq. wt. of silver bromide].

13. A metal forms three volatile chlorides containing 23·6, 38·2 and 48·3 per cent of chlorine respectively. The vapour densities of these chlorides (H=1) are 74·6, 92·9, and 110·6 respectively. Find the exact atomic weight of the metal and the formulæ of its chlorides.

[114·8; MCl, MCl_2, MCl_3]

14. The fluoride of an element is found to contain 59·067 per cent of fluorine (at. wt. 19) and its vapour is about 6·7 times as heavy as air at the same temperature and pressure. Determine the equivalent weight, atomic weight and valence of the element (Density of air at N. T. P. is 0·00129). [13·2; 79·6]

15. A metal is found to form two chlorides which yield on analysis 46·37 and 50·91 per cent of the metal. What is the least value of atomic weight that is possible for the metal. [184·2]

16. Tungsten trioxide contains 79·317 per cent of tungsten and the ratio WCl_6 : WO_3 is 100 : 58·487. Calculate the atomic weights for tungsten and chlorine. [183·99; 35·46]

17. Potassium perrhenate is isomorphous with potassium permanganate ($KMnO_4$) and it contains 64·37 per cent of rhenium. Calculate the atomic weight of rhenium. (K—39) [186·3]

18. Ferric alum and common alum are isomorphous and the former contains 11·09 per cent of iron and 25·45 per cent. of sulphur dioxide (SO_2) while the latter contains 5·68 per cent of aluminium and 27·01 per cent of sulphur dioxide (SO_2). Calculate the atomic weight of aluminium given the atomic weight of iron equal to 55·84, without assuming the formula for alum. [26·95]

19. An element x forms a chloride which contains 29·34 per cent by weight of chlorine and is isomorphous with potassium chloride. Calculate the atomic weight of x and explain clearly the theoretical principle you use in your calculation. What other experiments would you suggest to confirm the value of the atomic weight. [85·5]

20. A new element has only one isotope. Which one of the two atomic weights, one calculated on the conventional way and the other calculated on the physicist's scale, is higher. Discuss the principle.

CHAPTER XXV

ELEMENTARY PARTICLES: RADIOACTIVITY

Introduction--Dalton's concept of the atom as a minute indivisible mass, however satisfactory it might have been in explaining the laws of chemical combination and in bringing order in the divergent realms of chemistry, cannot be regarded as an ultimate solution of the problem of atomic structure. In absence of definite evidence, the chemists had to remain satisfied with this 'cannon-ball' theory of the atom, but now and again science in its onward march met with discoveries which were definite sign-posts pointing infallibly to some kind of planned internal organization for the atoms.

A new era was ushered in by the discovery of the first subatomic particle, the electron in 1898 by J. J. Thomson which was followed up by a succession of significant discoveries in a few related fields, the most important of which are (a) *the study of discharge through rarefied gases*, (b) *the phenomenon of radioactivity*, (c) *the study of spectra, and* (d) *atomic disintegration*. Some of these will be briefly discussed with special reference to the part they have played in the development of the current concept of the atom.

The Passage of Electricity through Gases—If a high potential is applied across a volume of gas at low pressure (0·01 to 0·001 *mm*), the electric discharge that takes place embodies some peculiar features. The cathode emits at right angles to its surface a stream of rays, called *cathode rays*, which travel in straight lines and produce strong fluorescence at the point of the glass wall where they impinge. If an apparatus as shown in
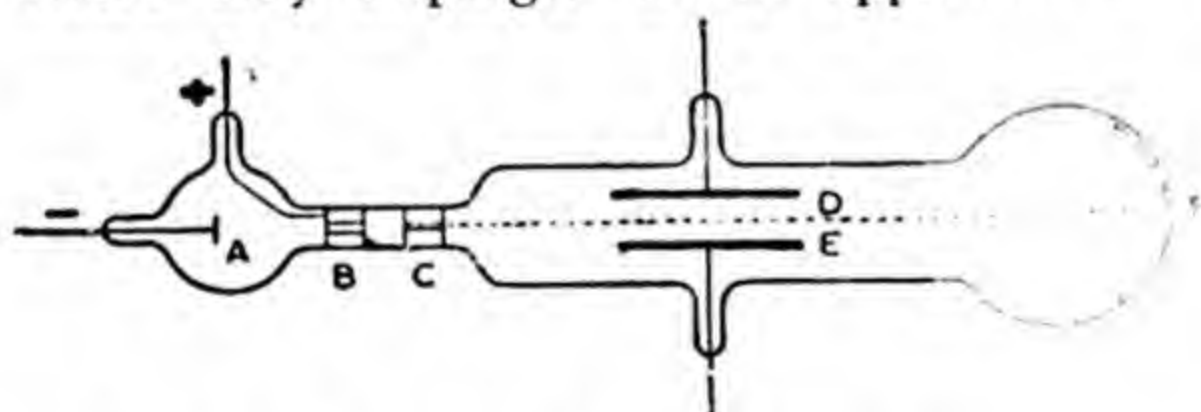
Fig. 112—Discharge through rarefied Gases.

Fig. 112 is used, the cathode rays will travel through the slits B and C and will produce a fluorescent spot at F. That the cathode rays consist of material particles is strikingly proved by the fact that on being allowed to fall on a suitably placed vane they can make it rotate about its axis. These material particles were found to be negatively charged and were called electrons and thus, cathode rays are simply a continuous stream of these electrons moving with high speed.

Determination of *e/m* **of Electrons**—With the above apparatus the ratio of charge, *e* to mass, *m* of the electron can be

determined. If a magnetic field, H is applied at right angles to the plane of the paper, the swarm of electrons being virtually an electric current, will get deflected at right angles to the field H so that the following relation holds,

$$H. e. v. = mv^2/r \quad \dots \quad \dots \quad \dots \quad (1)\text{-XXV}$$

where, r is the radius of curvature of the path and v, the velocity of the electrons. If an electric field, X is applied between the two plates, D and F so as to exactly counterbalance the magnetic deflection, we shall have

$$H e v = X e ; \text{ or, } v = X/H \quad \dots \quad \dots \quad (2)\text{-XXV}$$

whence v is known, and on substitution of this value of v in equation (1) wherein all the other terms are experimentally measurable, the ratio e/m becomes known.

The value of e/m comes out to be 1.769×10^8 coulombs per gram and the most important point is that irrespective of the gas used in the discharge tube, the same value of e/m is obtained. Hence, it is concluded that *electrons are the common constituent of all matter*.

Determination of the Charge of an Electron —The charge of an electron can be measured if the electric effect on it can be balanced against some effect which is uninfluenced by electric charge, such as gravitational effect. This was done by Millikan (1911) by absorbing electrons in oil drops and balancing the gravitational attraction on these against an applied electric field.

The main features of Millikan's apparatus are shown diagrammatically in Fig. 113. Oil drops produced by an atomiser, A are allowed to get into the space, A between the two electrodes. C and D. Ions are produced in the space, A by X-rays through a side window, and they get absorbed in the oil drops. By observing the velocity of settling of a drop under gravity and
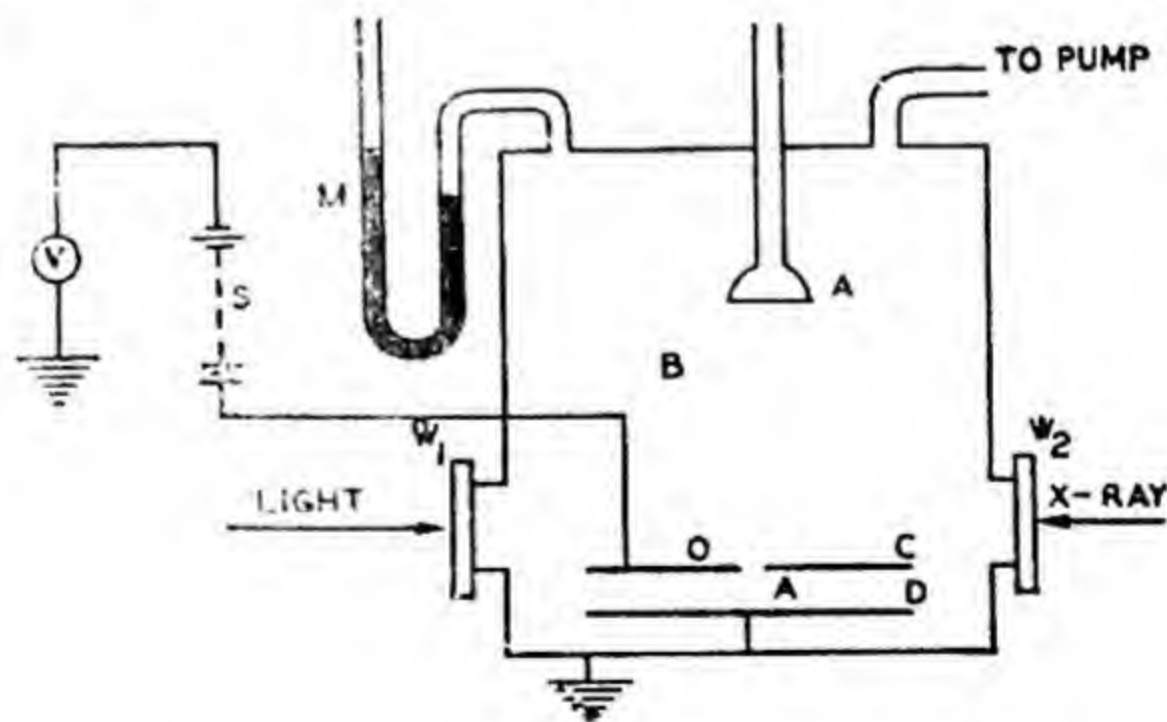
Fig. 113—Millikan's Oil Drop Experiment

the velocity of upward rise under the influence of an applied electric field between C and D the charge on the oil drop can be calculated. Millikan observed the charge on an oil drop to be a

variable quantity which is always an exact multiple of the electronic charge, e. The most recent value of the electronic charge is 4.802×10^{-10} e.s.u. or 1.602×10^{-19} coulomb. It is a striking fact that this value is also numerically equal to the charge of a monovalent ion. Since, an electric charge less than that on an electron is never found, this amount of electricity is called *unit charge*, e.

$$e = 4.802 \times 10^{-10} \text{ electrostatic units}$$
$$= 1.602 \times 10^{-19} \text{ coulombs}$$

Mass of an Electron—From the above-determined values of e/m and e of an electron, the mass, m is easily calculated and comes out to be 9.10×10^{-28} gram which is about 1/1800 times the weight of a hydrogen atom. Now, we have seen in the preceding paragraph that the negative charge of an electron is equal to the positive charge of a hydrogen ion. Hence, *an electron is about 1/1800 times as light as a hydrogen ion, but has a charge numerically equal to that of a hydrogen ion*.

Proton—We have seen that electrons are the common constituent of all matter. Since matter as a whole is electro-neutral, these electrons must have a positive counterpart, which was ulimately identified as the positively charged hydrogen atom this being the lightest positively charged *stable* material particle ever met with, and was named '**Proton**'. That protons are a universal constituent of matter is proved by the nuclear disintegration experiments of Rutherford (1919) who found that by bombardment of some lighter elements with α-particles, protons are set free. Thus a proton has a mass practically equal to that of a hydrogen atom but has a positive charge numerically equal to the negative charge on an electron.

Neutron—It was observed in 1930 that a very penetrating type of ray is emitted when beryllium is bombarded by fast α-particles. Irene Curie and F. Joliot (1931), Chadwick (1932) and others examined the rays and found them to be composed of particles having *no electric charge and a mass equal to that of hydrogen atoms*. These were called neutrons. With the discovery of neutrons, the then prevalent idea that the nuclei of atoms consist of protons and electrons which was already proving unsatisfactory for various reasons, was immediately discarded and it was postulated that only protons and neutrons build up the nucleus. Since neutrons have zero charge, it is sometimes considered as an element of zero atomic number.

Constituents of Matter—So far we have discussed only three elementary particles, electron, proton and neutron. Many other elementary particles such as positron, antiproton, antineutron, mesons of various types, neutrino, etc. have been discovered and a few more are certain to be discovered yet. However, ordinarily it seems that only five particles are involved as atomic constituents of which three *viz*. electron, proton and neutron are structural units

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and two *viz.* the photon or light quanta and the mesons, are cements for these building blocks for atoms. So only the electron, proton and neutron, the mass and charge of which are included in the table to follow are of importance to chemistry.

We should not be led to think however that our familiar world is the only type of matter possible. The discovery of anti-proton has suggested the possibility of existence of antimatter, in which the nucleus of an atom is negatively charged and is surrounded by positrons. Even if whole galaxies are made of it, we would never know, as its optical properties would be indistinguishable from ordinary matter. Further in some stars it is known that nuclei of atoms are fused into dense matter called *plasma* which may be thousands of times heavier than ordinary matter (a spoonful weighing some tons or more).

POSITIVE *particles* (charge $= + e$)	NEUTRAL *Particles* (Charge $= 0$)	NEGATIVE *Particles* (Charge $= -e$)
Proton *mass* $= 1 \cdot 00758$	**Neutron** *mass* $= 1 \cdot 00897$	Anti-proton (Lately detected)
Positive MESON *mass* about $0 \cdot 1$	(Neutral Meson not known)	Negative MESON *mass* about $0 \cdot 1$
POSITRON *mass* $= 0 \cdot 000548$	NEUTRINO *mass* about $0 \cdot 0005$ (existence surmised and lately proved)	**Electron** *mass* $= 0 \cdot 000548$

Mass given in Physicist's atomic weight scale, $O^{16} = 16 \cdot 0000$.

Positron—While studying the interaction of *cosmic rays* (a kind of extremely penetrating ray coming from outside the earth) with matter, Anderson (1932) observed that particles *equal in mass to an electron but carrying unit positive charge* were produced; they were called **Positrons.** Positrons were later found to be also produced by bombarding lead, aluminium, etc. by the highly penetrating γ-rays from radioactive thorium C. The discovery of positrons has not however, markedly influenced our view on atomic structure since positrons are very unstable with a life period of about a millionth part of a second.

RADIOACTIVITY

Introduction — In 1896 Becquerel observed that uranium minerals continuously emit a kind of radiation, which can penetrate thin sheets of matter, can affect a photographic plate in the dark and can ionise a gas through which it passes, *i.e.* can make the gas conductor of electricity. Thus, if a radioactive material is kept near a photographic plate even as originally packed, the plate is 'fogged'. A charged gold-leaf electroscope gets also quickly discharged near a radioactive material and these may be used as simple tests for detecting radioactivity. This property of emitting

active radiation was called radioactivity. Later researches have established that these active radiations emanate from the nuclei of atoms which are basically unstable and break down into new atoms with expulsion of these active radiations and release of a tremendous amount of energy. We shall shortly study a little closely these radiations as also the nuclear transformations which originate these radiations.

It was discovered shortly after, that not only uranium but many other elements particularly the then newly discovered element radium possessed radioactive property to a pronounced degree. It was rightly guessed that radioactivity is a nuclear phenomenon, since the rate of radioactive change is not influenced by any change of imposed conditions, such as temperature, pressure, chemical combination, etc.

Radiation from Radioactive Materials—The application of electric or magnetic field reveals the fact that the radiation emitted by radioactive materials is composite in nature. The rays when subjected to the action of an electric or magnetic field (Fig. 114), are divided into three groups, one called α-rays behaving like positively charged particles, another called β-rays behaving like negatively charged particles and the third group called γ-rays remaining uninfluenced by electric or magnetic field. Their properties are summarised below.
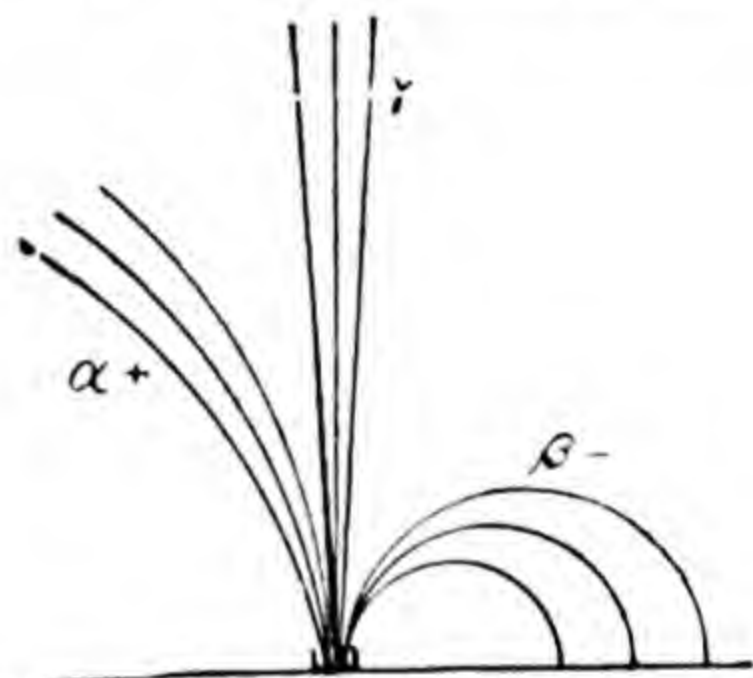
Fig. 114.—Deflection of rays from radium in a magnetic field.

α-**Rays**—These are material particles of mass equal to four (hydrogen atom as unit) carrying 2 units of positive charge, and have the least penetrating but the greatest ionisation power. Rutherford proved conclusively by *spectrographic* method that α-*rays are really doubly charged helium atoms.* Since α-rays are continuously emitted from radium, uranium, etc. we encounter the novel fact that an element helium is produced from another element.

β-**Rays**—These are more penetrating than α-rays and carry unit negative charge. They are really *a stream of electrons* shot out from the radioactive material with a very high velocity almost approaching that of light.

γ-**Rays**—These are non-material rays in the classical sense of the term, being hard X-rays with high penetrating power, being identical with X-rays produced in an X-ray tube operated at a very high voltage.

Nature of Radioactivity of Radium—If a radium salt is dissolved in water under low pressure, a gas is evolved. This gas,

called radon, is an inert elementary substance and has an atomic weight 222. After recovery of the gas the radium salt is found to have lost quite a good portion of its radioactivity but after some time the activity is regenerated and a further quantity of radon gas is recoverable. Hence, we see that the gas, radon which is far more radioactive than radium is continuously being
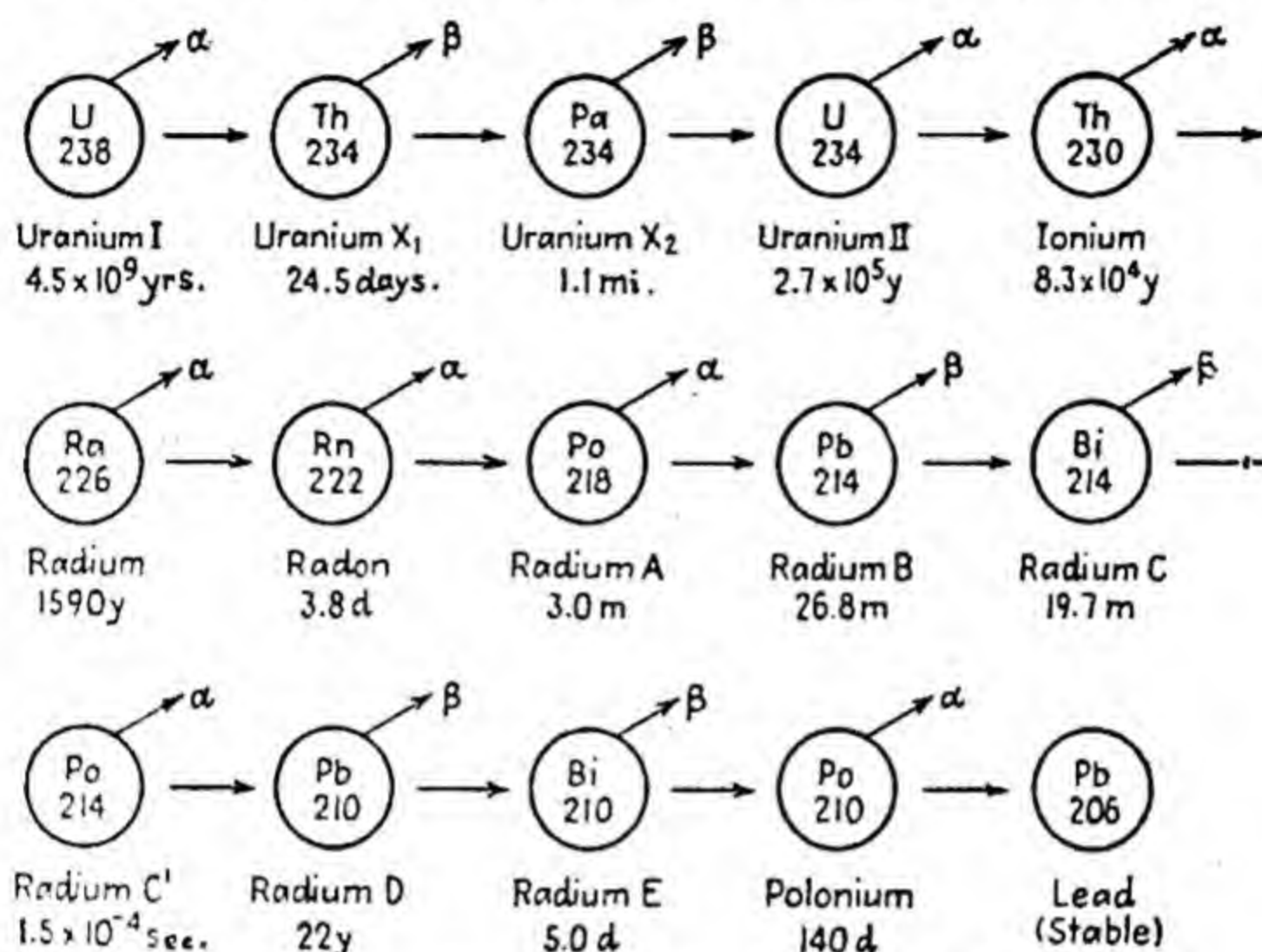
Fig. 115—Radioactive Decay Series of Uranium

formed from radium and remains encased in it, and the usually observed strong radioactivity of radium is mostly due to the presence of this enclosed radon gas. Since radium has an atomic weight, 226 and radon, 222 and α-particles are doubly charged helium atoms of mass 4, the conclusion is obvious that radium is continuously breaking down into two other elements, radon and helium. This was the first instance of an actual transmutation of element occurring in nature, under conditions uncontrollable by all means at our disposal.

On closer examination it is noticed that radon gas is itself radioactive and shoots out α-particles. It passes through successive stages of disintegration giving rise at each stage to elements which are themselves radioactive and is ultimately converted into lead. This series of transformation is shown above, where each element could be observed to emit either an α- or a β-particle and as a result is converted into the next element as named in the series.

All these intermediate products are definite elements differing from ordinary elements only in the fact that their atoms are unstable and shoot out either α-particles or β-particles to be converted into another element. In fact, Ra A, Ra B, etc. are isotopes of hitherto known elements and these names are of historic importance only. A more intensive enquiry has shown

that radium is not the ultimate progenitor of this series but that it is itself derived from uranium through a number of steps as recorded in Fig. 115.

Radioactivity as Nuclear Transformation—From what has appeared in the preceding sections, it is abundantly clear that radioactivity is a nuclear property. In fact, radioactivity can be defined as a transformation of the nuclei of one atom into another with the release of a tremendous amount of energy, and usually accompanied by expulsion of nucleons, *i.e.* particles obtainable from the nucleus. The expelled particles are helions (α-particles), electrons (β-particles) or photons (γ-particles) for naturally radioactive atoms but can also be neutrons, positrons, etc. for artificially radioactive atoms. Thus we can represent the conversion of uranium into thorium (the first step in Fig. 115) by the chemical equation—

$$_{92}U^{238} = \,_{90}Th^{234} + \,_{2}He^{4}$$
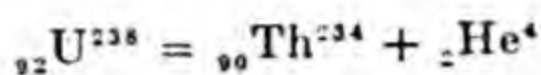
In the above equation uranium ($_{92}U^{238}$) is called the *parent* isotope and Thorium ($_{90}Th^{234}$) is called the *daughter* isotope.

The Three Natural Radioactive Series—The uranium series (Fig. 115) of which radium is a very well-known member is not the only radioactive series met with in nature. Two other series, one called *Thorium series*, beginning with Th^{232} and another called *Actinium series*, beginning with U^{235} are also encountered in nature (Fig. 116). The Thorium series is also called $4n$ series because the mass number of the member elements are exact multiples of 4 : similarly, the uranium series is called $4n+2$ series and the actinium series, $4n+3$. The $4n+1$ series has not been found in nature presumably because the half life of the longest living member is too small to have lasted out the geological age of the earth. In fact, many radioisotopes do not exist in nature now, though they certainly existed before, owing to too short half-life period.

It is of interest to note that some common elements, ordinarily considered nonradioactive, contain radioactive isotopes in small proportion. A well-known example is ordinary potassium which contains the radioisotope $_{19}K^{40}$ (half-life, 2×10^{9} years) to the extent of as high as 1 atom per 600 or so, and therefore ordinary potassium is distinctly radioactive.

Rate of Radioactive Change—The rate of radioactive change for all radioactive elements follows a simple unimolecular law (*vide* P. 313), *i.e.* in any given time a certain fraction of the total number of atoms decomposes with emission of α or β-particles. This can be expressed algebraically as follows—

$$-\frac{dN}{dt} = \lambda N \quad \text{or} \quad N = N_0 e^{-\lambda t}$$

where N is the number of particles present after time t and N_0 is the total number of particles to start with, and λ is a constant whose reciprocal is called average life. The rate of radioactive decomposition is more conveniently expressed as the *half-life*

period or time of half decay which is the time necessary for the radioactive disintegration of half of a given mass of an element. The half-life period of radium is 1590 years ; for other radioactive elements this may vary from a few million years or more to a fraction of a second (Fig. 115).

Age of the Earth —Since half-life of uranium is about 4 billion years (4×10^9 years) which is unaffected by any external factor and since the ultimate product of this series is lead (Pb^{206}) (*vide* Fig. 115), a determination of the ratio of uranium to lead (Pb^{206}) of a uranium mineral gives an idea of the age of the mineral, *vis-a-vis* the age of the earth. Thus, such minerals serve as *geological clocks*, wherein is recorded the time of formation of earth. By such means it has been found that our earth started to have its birth about 2 to 5 billion (2 to 8×10^9) years ago.

Position of the Radioelements in the Periodic Table —It is evident from Fig. 115 that radium, an element of Group II is

Fig. 116—Radioactive Displacement Law.

converted by the emission of an α-particle into the inert gas, radon, a zero group element *i.e.* the expulsion of an α-particle displaces the element two steps backward in the periodic table. Similarly,

it is observed that by the emission of a β-particle, the position of the new element is one step forward in the periodic table. This is embodied in the "Displacement law" according to which emission of an α-particle produces an atom two steps backward and a β-particle, one step forward in the periodic table. This is shown for uranium series in Fig. 116. The displacement law is readily explained on the assumption that the nuclear charge determines the position of an element in the periodic table and that each element has one unit more of positive charge than the preceding element.

An interesting conclusion may be drawn from the above. Suppose an element loses an α-particle and two β-particles consecutively; it will revert to its initial position but will be lighter in mass by four. So, these two elements will be identical in chemical properties, though differing in mass and such elements are called *isotopes*. Thus, the discovery of such a large number of new elements from a study of radioactivity introduces no difficulty in assigning positions in the periodic table. They either occupy vacant spaces in the periodic table or are isotopes of already known elements and so share places with them.

Artificial Radioactivity. Nuclear Bombardment—In 1932 F. Joliot and Irene Curie bombarded boron with fast α-particles and observed an extremely remarkable result. They found that this has brought about a nuclear reaction producing an isotope of nitrogen of atomic mass 13 with liberation of neutrons. The reaction can be symbolically expressed as

$$_5B^{10} + _2He^4 \; (\alpha\text{-}particle) \longrightarrow \; _7N^{13} + _0n^1 \; (neutron)$$
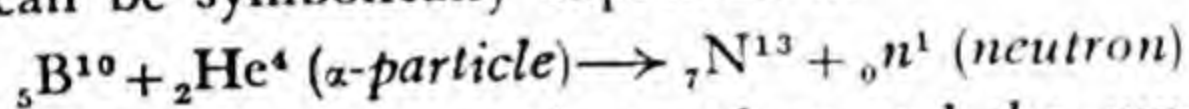
where the subscripts are atomic numbers and the superscripts are atomic masses (Note that there is conservation of both the subscripts and the superscripts in such equation ; also note that some authors write the superscript *i.e.* atomic mass as a prefix, as for example, $^{10}_5B$ instead of our $_5B^{10}$).

This result is of great importance for a number of reasons. *Firstly*, this led to the discovery of neutrons. *Secondly*, this conclusively proved the reality of transmutation of elements, though Rutherford much earlier in 1919 brought about another transmutation by bombarding nitrogen with α-particles into oxygen of mass 17 as shown below—

$$_7N^{14} + _2He^4 \; (\alpha\text{-}particle) = \; _8O^{17} + _1H^1 \; (proton)$$
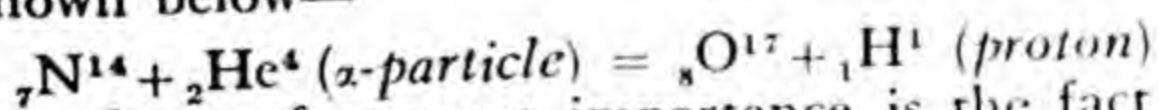
Thirdly and perhaps of greatest importance is the fact that the nitrogen isotope produced *viz.*, $_7N^{13}$, is itself radioactive and decays according to the following scheme with a half-life of about 10 minutes with emission of the short-lived positron and being converted to carbon of mass 13.

$$_7N^{13} \longrightarrow \; _6C^{13} + \beta^+ \; (positron)$$
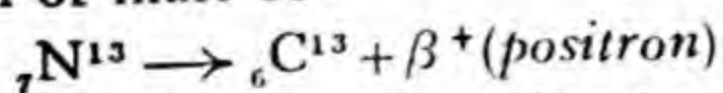
Thus for the first time a radioactive isotope of an ordinary element was produced. Such radioactivity is called *artificial* or *induced radioactivity*. This has been followed up by the prepara-

tion of a few hundreds of such artificial radioactive isotopes rang-
ing from the lightest tritium (*i.e.* hydrogen of mass 3, $_1H^3$) to the
heaviest transuranium elements using various types of missiles,
viz. neutron, $(_0n^1)$, proton $(_1p^1)$, deuteron $(_1d^2)$, α-particle $(_2He^4)$,
etc. Some typical examples of artificial radio-isotopes obtained by
bombarding ordinary elements with various types of particles, are
listed in the table with their method of preparation and other
relevant data.

Method of Production (nucleus & missile)	Radio element produced	Characteristic Radiation	Half-life period
$_1D^2 + _1d^2$	$_1H^3$ (Tritium)	β (electron)	12 years
$_6C^{13} + _1d^2$	$_6C^{14}$	β	5700 years
$_5B^{11} + _2He_4$		β	,, years
$_6C^{12} + _1p^1$	$_7N^{13}$	$\beta + (positron)$	9·9 mi
$_{11}Na^{23} + _1d_2$	$_{11}Na^{24}$	β	14·8 hours
$_{15}P^{31} + _0n^1$	$_{15}P^{32}$	,,	14·3 days
$_{35}Br^{79} + _0n^1$	$_{35}Br^{80}$	β	18 mi
$_{79}Au^{197} + _0n^1$	$_{79}Au^{198}$	β	2·7 days

Since the bombarded atom very often contains a number of
isotopes, and since a number of nuclear reactions often take place
simultaneously, the net reaction usually becomes very complicated
and the products become often difficult of identification. A target
such as natural gold is very convenient to work with as it contains
only one isotope. For example, by bombardment with neutron
it undergoes an n, γ reaction (*i.e.* neutron bombardment, expul-
sion of γ-rays) followed by electron emission (*vide* table, last line)
to produce mercury (Hg^{198}) as a single isotope [(*i*) & (*ii*)].

(i) $_{79}Au^{197} + _0n^1 = _{79}Au^{198} + \gamma$;   (ii) $_{79}Au^{198} = _{80}Hg^{198} + _{-1}\beta^0$ (*electron*)
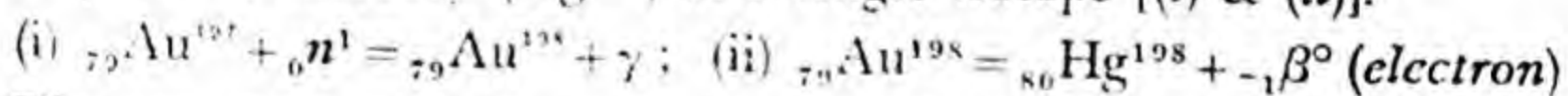
The spectrum of this single isotope of mercury contains lines of
very well-defined wavelength which are nowadays utilised as the
most accurate standard of length.

Application of Radioisotopes —Any radioisotope is practi-
cally identical in chemical properties with its non-radioactive
counterpart, but the former atoms are self-signalling in the
sense that they signal their presence in presence of Geiger
counters or other sensitive detectors of radioactivity even when
present in minutest quantity, which is far beyond the detec-
tion limit of ordinary analytical methods. Even single atoms
can be detected. So, the radioisotopes serve as a very
powerful tool to follow the fate of a certain element in any
physical, chemical or biological process. The method consists
in using 'labelled' or 'tagged' compounds, *i.e.* samples of a com-
pound containing some proportion of molecules which contain the
radioisotope of the element in question and following *i.e.* tracing
the path of the 'labelled' atom by radioactivity-detectors. Such
methods are hence called **'tracer techniques'**. Sometimes when

a suitable radioisotope is not available, molecules are tagged with non-radioactive isotope, as for example, deuterium for hydrogen, and O^{18} for oxygen, and the tracing is done with mass spectograph. Some typical applications of radioisotopes are briefly listed below—

(1) **Chemical Analysis**—It has been said that by radio-activation analysis "needless in chemical haystacks" can be precisely picked up. One of the methods is to irradiate the sample by a neutron source and identify and estimate the expected radio-isotope by its half-life and its radioactivity. Submicro quantities of the order of 10^{-8} gm or less of many elements can be estimated by this method.

(2) **Standard of length**—Production of single isotope of mercury by bombarding gold with neutrons, whose spectral lines would serve as standard of length, has been already described.

(3) **Low Solubility and Vapour Pressure**—Since extremely small quantities of radio-elements can be easily measured, it is easy to determine very low solubility values by experimenting with a sample containing a radioisotope. Thus solubility of lead chromate can be easily measured by using a sample containing some radioactive lead.

(4) **Isotope Dilution Technique**—We can illustrate the method by a typical example. For example, if we desire to know the total volume of blood in the body we can add a small volume of a radioactive solution and a short while after measure the radioactivity of a known volume of blood. The ratio of the total radioactivity injected to the radioactivity per cc of the blood gives the total volume of blood in the body.

(5) **Mechanism of Reaction**—We may illustrate by a typical example. Suppose, we desire to know if during hydrolysis of an ester the cleavage occurs at the C-O bond or at the O-R bond. We can use H_2O with a 'labelled' oxygen and find out if the 'labelled' oxygen appears in the acid or the alcohol. It is found that the 'tagged' oxygen appears in the acid and so it is concluded that a C-O bond is severed in ester hydrolysis.

$$R\ CO\ OR_1 + HOH \longrightarrow R\ CO\ OH + R_1OH$$
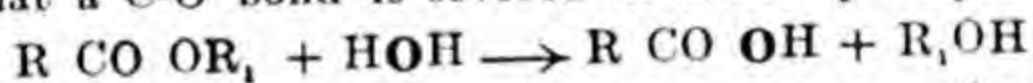
(6) **Miscellaneous Applications**—Various other applications of tracers in physics, chemistry, biology, medicine, etc., are increasingly being made to obtain results which are otherwise unattainable, to name a few, self-diffusion constant of metals and ions, assimilation of N, P, C, etc. in biological systems, determination of age of old specimens of wood, frictional wearout, etc. (see also p. 212). Some medical applications, such as radiophosphorus (P^{32}) in blood leukemia, radioiodine (I^{131}) in thyroid disorder, radiations from Ra, radon, etc., in cancer, and so on, have shown very promising results.

Exercises

1. Name at least two fundamental subatomic particles; describe their discovery and discuss their properties.

2. Describe how the ratio of charge to mass of an electron was determined by Millikan. How does this value compare with that of the hydrogen ion. Why is this charge called unit charge.

3. What is radioactivity? Given a piece of mineral, how can you determine by simple experiments if the mineral is radioactive.

4. Write short notes on :—(i) a-rays, (ii) Half-life of radioactive decomposition, (iii) radioactive equilibrium, (iv) atomic weight of lead in radioactive minerals, (v) tracer technique, and (vi) radioactive displacement law.

(5) Give a brief account of artificial radioactivity. Cite some applications of induced radioactivity, with special reference to problems connected with mechanism of chemical reactions.

(6) Why is natural radioactivity mostly limited among heavier elements? Give one or two examples of the occurrence of radioactivity among lighter elements.

NUCLEAR THEORY OF THE ATOM

Scattering of α-particles by Matter —Very definite indications were obtained by Rutherford (1911) on the structure of atoms, from experiments on the passage of α particles through thin metal foils. The majority of the α-particles pass through almost unchanged in direction, except a very small proportion which are violently deflected from their path. This is shown schematically in Fig. 117, where the dark dots are electrons
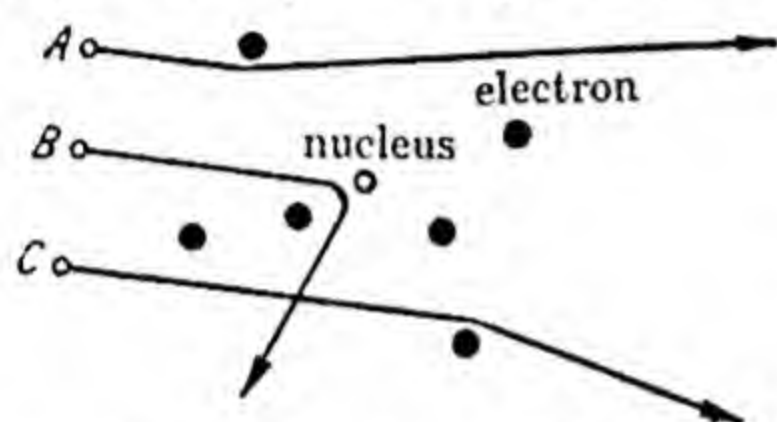

and the unshaded circle the nucleus (in reality it is much smaller). The α-particles A and C pass with little deflection whereas B which suffers almost head-on collision, is violently deflected. For example using a gold foil 0·004 mm thick one α-particle in 20,000 was deflected through 90° or more. From this Rutherford concluded that

Fig. 117—Path of α-particles through an atom (black dots are electrons and the circle is the nucleus, not to scale).

the space occupied by an atom is practically void allowing unobstructed passage to fast-moving α-particles (and also β-particles) except for a very small positively charged nucleus occupying a negligible portion of the total volume ascribed to the atom. He made an approximate estimate of the nuclear charge which came out to be approximately equal to half the atomic weight. In 1913, van der Brock suggested that the nuclear charge is equal to the serial number of the atom in the periodic table, this serial number being designated later as atomic number.

X-ray Spectra of Elements —The importance of atomic number, however, was first conclusively demonstrated on experimental basis by Mosley (1913) from a study of the X-ray spectra of the elements. If a stream of cathode rays is made to strike an anticathode made of a particular element, a stream of X-ray, containing various lines called K_α, $K\beta$...............L_α, $L\beta$, etc., characteristic of this element is produced. Mosley determined the wavelengths of some of the principal lines in the X-ray spectra of various elements and found that if the square root of frequency of any particular line, say, K_α in the X-ray spectrum of the elements is plotted against their atomic number a smooth straight line is obtained, whereas if plotted against the atomic weight the resulting curve is an irregular zigzag one. His actual results can be expressed by the equation,

$$\sqrt{\gamma} = a\,Z - \beta \qquad \dots \qquad \textit{Mosley's equation.}$$

where γ is the frequency, Z is the atomic number and a and β are constants. Conversely, knowing the X-ray spectra of an unknown element, the above equation can be used for determining its atomic number.
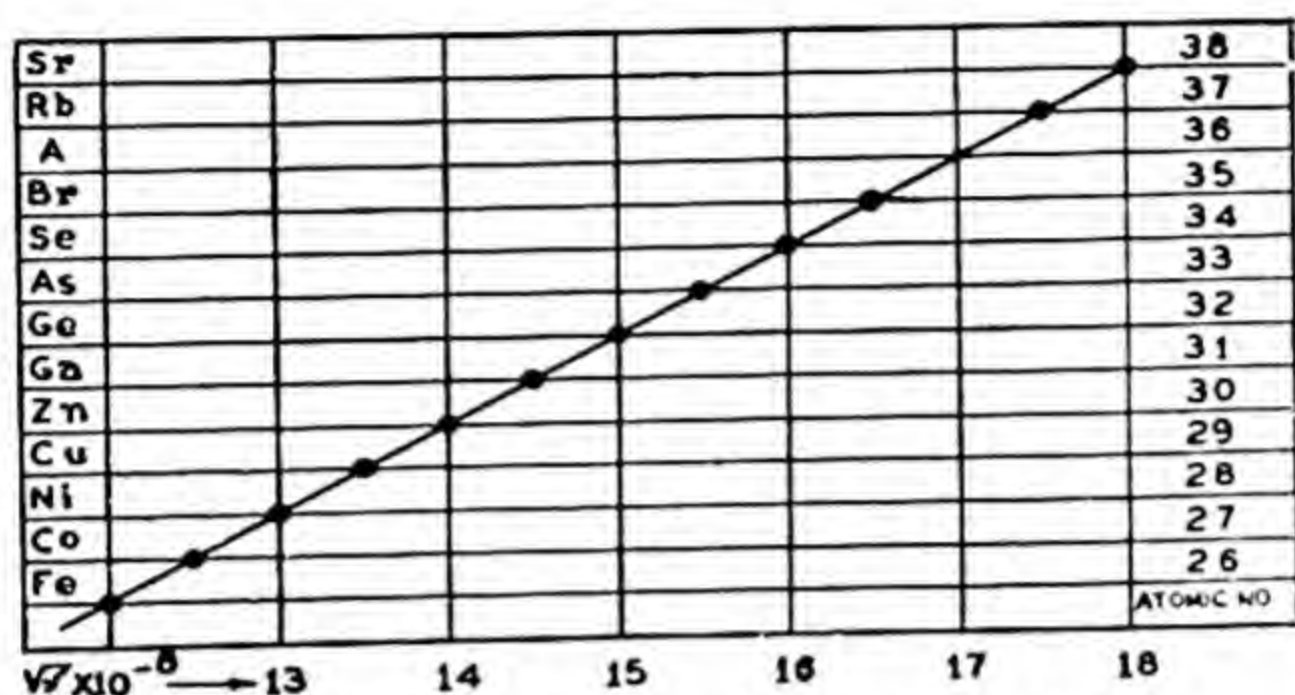
Fig. 118—Mosley plot of X-ray K_α line.

A Mosley plot for some lighter elements is shown in Fig. 118 to illustrate the linearity of atomic number and square root of frequency of the K_α line. From such a plot Mosley concluded: "There is in the atom a fundamental quantity which increases by regular steps from one atom to the next. This quantity can only be the charge on a central positive nucleus". Thus Mosley identified the atomic number as the nuclear charge of the atom.

Thus following Mosley we find that the fundamental characteristic of an element by which its other properties are determined is not the atomic weight but the atomic number, which latter is equal to the nuclear charge and we have here a simple experimental method of determining atomic number. All isotopes of the same element were found to have the same atomic number irrespective of their atomic weights, and very closely related elements viz. the rare earths were proved to be distinct elements of well-defined atomic number and so, the possible number of rare earths about which there was a little confusion at the time was finally fixed. Also, the classical anomaly in atomic weights of such pairs as Co & Ni, Te & I, etc., with regard to their position in the periodic table disappeared as their atomic numbers were found to be in agreement with their position in the Periodic table.

Rutherford Theory of Atomic Structure —We owe to the genius of Rutherford our basic idea of the structure of the atom. The experiments by Rutherford and his associates on the scattering of α-rays by matter as discussed in our opening paragraph indicated atoms to be void matter with a positively charged nucleus. From this Rutherford in 1911 conceived the idea that *the atom consists of two parts, a very small positively charged nucleus occupying a negligible fraction of the total volume of the atom, and an extra-nuclear part containing a number of electrons*

just sufficient to make the atom as a whole electroneutral. It was suggested by van der Brock that the positive charge of the nucleus is equal to its atomic number, *i.e.* the serial number of the atom in

Fig. 119—Lord Rutherford [1871-1937]

the periodic table, and this was almost immediately confirmed by the now classical work of Mosley on X-ray spectra of elements as described in the previous para.

The composition of the nucleus was originally surmised to be wholly of electrons and protons but with the later discovery of neutrons, evidences both theoretical and experimental piled up to show that electrons are not present in the nucleus, and the latter contains only protons and neutrons. One of the simplest facts that rules out the existence of electrons in the nucleus, is that the volume of an electron is much bigger than that of the nucleus. Paradoxically however, a nucleus can expel electron out of it (β-ray activity) or is capable of absorbing electrons (K-capture).

Bohr (1913) applied this idea in conjunction with quantum theory with conspicuous success in quantitatively deriving the lines in the spectra of the hydrogen atom and this led to a wide acceptance of the Rutherford model of the atom. Further refinements were gradually introduced in this picture as a result of theoretical development in quantum mechanics and accumulation of more precise experimental data.

Size of the Atom and the Nucleus—It is imperative that the students should have a clear notion of the atomic and related dimensions. Atoms are generally 2 to 5 Å (Ångstroms) in diameter ($1Å=10^{-8}$ cm). The nucleus is about one-ten thousandth times smaller in diameter, and the wavelength of visible light is about one thousand times longer.

This is easily visualised by appreciating that if the atomic diameter is as long as a football field, the nucleus of the atom would occupy a cross section almost equal to that of a pea. In this magnified unit, the wavelength of visible light which is only a few hundred millimicrons ($m\mu$), will appear to be long enough to cover a distance of about hundred miles.

Some interesting facts come out if we calculate from the above figures the relative volume and density of the nucleus. Since the nuclear diameter is one ten thousand times i.e., 10^{-4} times, its volume is cube of this quantity i.e. 10^{-12} times. In other words, *the nucleus occupies a volume of about 10^{-12} i.e., one million millionth of the volume of the atom* and so, the inside of an atom is veritably an empty space and hence is often likened to a miniature solar system.

Since the whole mass of the atom resides in the nucleus, it is evidently this many times as heavy as the atom as well, which on conversion to our ordinary units would be of the order of some millions of tons per c.c. That this is nothing fantastic is indicated by the fact that in some of the stars, for example in Sirius, where the nuclei are mostly stripped of their electrons owing to high temperature, the average density is known to be over a ton per cubic inch.

Nuclear Structure—The main features of atomic structure being established by the Rutherford model of the atom we now discuss the detailed structure of its two regions, viz., the nucleus and the extra-nuclear part.

The nucleus of an atom is composed of a *dense packing of protons and neutrons* to give it the necessary charge and mass. Since electrons have very little weight in comparison with protons and neutrons, the weight of the nucleus may be regarded with fair approximation to be equal to the weight of the atom itself. As already pointed out, the volume of the nucleus is negligible in comparison with the volume of the atom, and the positive charge on the nucleus is equal to its atomic number. Since both protons and neutrons have unit mass and only the former carries a charge, the nuclear structure according to this scheme is easily framed on the following basis.

(i) *The number of protons in the nucleus is equal to its atomic number, since this will give the requisite positive charge.*

(ii) *The total number of protons and neutrons is equal to the mass of the atom.*

The composition of several nuclei is shown in the following table, where the atomic number and atomic mass are represented respectively by subscript and superscript to the symbol.

Element	Symbol	Atomic number, Z	Atomic weight, A	Number of Protons Z	Number of Neutrons A-Z
Hydrogen	$_1H^1$	1	1·008	1	0
Helium	$_2He^2$	2	4·003	2	2
Lithium	$_3Li^7$	3	6·940	3	4
Carbon	$_6C^{12}$	6	12·010	6	6
Nitrogen	$_7N^{14}$	7	14·008	7	7
Oxygen	$_8O^{16}$	8	16·0000	8	8
Chlorine	$_{17}Cl^{35}$	17	35·00	17	18
,,	$_{17}Cl^{37}$	,,	37·00	17	20

Summing up, if an element has an atomic weight A and an atomic number Z, the nucleus would contain Z protons and A—Z neutrons, and there would be also Z electrons in the extranuclear part rotating in definite orbits to make the atom electroneutral. This is illustrated below by some typical examples.
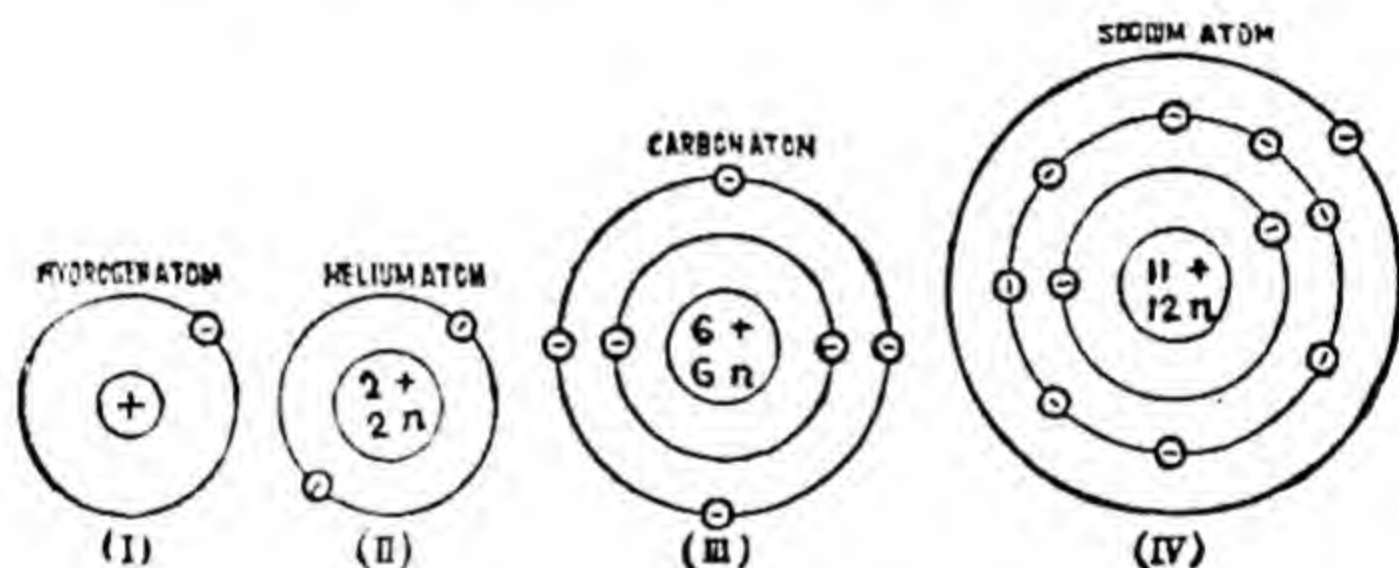
Fig. 120—Structure of Atoms

The hydrogen atom which is the first member of the periodic table and hence, has an atomic number unity, consists of only one proton in the nucleus and one planetary electron revolving round it (Fig. 120). The single proton in the nucleus accounts for the unit mass of the hydrogen atom, and gives it unit positive charge.

The lithium atom has an atomic number 3 and hence contains 3 protons in the nucleus to give a nuclear charge of 3 positive units. Since the atomic mass is 7, the nucleus also contains 4 neutrons. As the nuclear positive charge is 3, there are 3 electrons revolving round it. So, a lithium atom contains 3 protons and 4 neutrons in the nucleus and 3 electrons outside the nucleus.

The sodium atom of atomic number 11 and atomic weight 23 should therefore consist of 11 protons and 12 neutrons in the nucleus to give it the requisite charge and mass and should also have 11 extranuclear electrons (Fig. 120). The structures of a number of atoms are also shown in Figs. 120 and 121.

Arrangement of the Electrons: Electron Shells—We have discussed the structure of the nucleus in the preceding section and we now discuss about the arrangement of the electrons outside
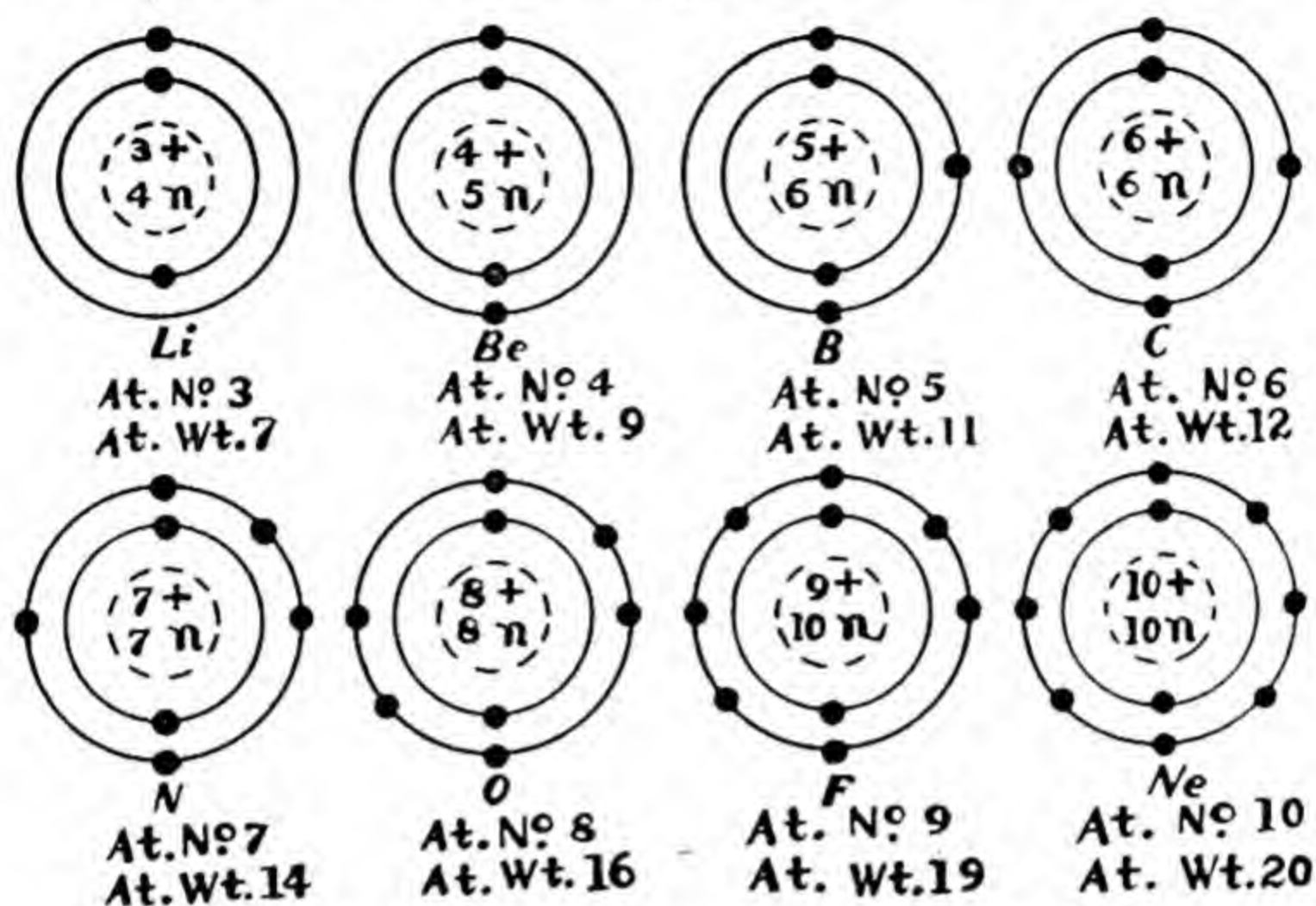
Fig. 121—Structure of Atoms of the First Period of the Periodic Table.

the nucleus. Most of our knowledge here has been obtained from a study of spectra, which being beyond our scope, we shall briefly present the final results.

The planetary electrons are arranged in *shells* or *rings*, also called *electronic levels* or *orbits* each of which can hold a definite number of electrons. The first shell, called K shell can contain a maximum of 2 ($=2 \times 1^2$) electrons, the second shell called L shell, $8(=2 \times 2^2)$ electrons, the third shell or M shell $18(=2 \times 3^2)$ electrons and so on.

Subshells of Electrons—Each shell (except the first or K shell) is divided into two to four subshells which are generally called *orbitals* and are designated as s, p, d and f orbitals. An s orbital can hold a maximum of two electrons and when filled up is written s^2; a p orbital may contain upto six electrons, written p^6; a d orbital ten electrons, written d^{10}, and an f orbital fourteen electrons, written f^{14}. In this notation the shell number precedes the orbital symbol; thus $2p^6$ stands for six electrons of p subshell (orbital) in the second, *that is*, L shell. The following table describes the electronic structure of the first forty five elements and the first eight are shown graphically without the finer classification of the electrons in the subshell in Fig. 121.

However, an electron does not enter the outermost ring only when the inner ring is filled up; electrons may be added to the outer ring even when the innermost rings are unsaturated. This particularly happens when the energy levels of the two

ARRANGEMENT OF THE ELECTRONS

Element (Atomic number)	K	L		M			N				O	Shell → Quantum Number & Orbital
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	
H (1)	1											
He (2)	2											
Li (3)	2	1										
Be (4)	2	2										
B (5)	2	2	1									
C (6)	2	2	2									
N (7)	2	2	3									
O (8)	2	2	4									
F (9)	2	2	5									
Ne (10)	2	2	6									$1s^2 2s^2 p^6$
Na (11)				1								
Mg (12)				2								
Al (13)				2	1							
Si (14)		10 electrons		2	2							
P (15)		(Neon core)		2	3							
S (16)				2	4							
Cl (17)				2	5							
A (18)				2	6							$1s^2 2s^2 p^6 3s^2 p^6$
K (19)	2	2	6	2	6		1					
Ca (20)							2					
Sc (21)						1	2					
Ti (22)						2	2					
V (23)						3	2					
Cr (24)		Core of 18 electrons				4	1					
Mn (25)		(Argon core)				5	2					
Fe (26)						6	2					
Co (27)						7	2					
Ni (28)						8	2					
Cu (29)	2	2	6	2	6	10	1					
Zn (30)	2	2	6	2	6	10	2					
Ga (31)							2	1				
Ge (32)							2	2				
As (33)							2	3				
Se (34)							2	4				
Br (35)							2	5				
Kr (36)							2	6				
Rb (37)							2	6			1	
Sr (38)		Core of 28 electrons					2	6			2	
Y (39)							2	6	1		2	
Zr (40)							2	6	2		2	
Nb (41)							2	6	4		1	
Mo (42)							2	6	5		1	
Tc (43)							2	6	6		1	
Ru (44)							2	6	7		1	
Rh (45)							2	6	8		1	

orbitals concerned, such as $4d$ and $5s$ levels, $4f$ and $5d$, etc. are somewhat close to each other. Thus, argon has a structure 2; 8 ; 8 ; or in notation, $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$, and in the next element potassium the additional electron instead of enriching the $3d$ orbital by one electron enters the $4s$ orbital giving potassium the structure 2; 8; 8; 1 i.e. $1s^2$ $2s^2p^6$ $3s^2p^6$ $4s^1$ where it will be noted that the third ring contains only eight electrons though its maximum saturation capacity is 18 electrons.

The same building-up process continues with the next element, calcium where also the extra-electron shows preference for the $4s$ orbital (see Table). With the next element, scandium however, a reorganization starts and electrons begin to be added to the inner unsaturated $3d$-orbital and this process of consolidation of the inner $3d$ orbital goes on right through the so-called iron transitional elements and is not complete until copper (ous) is reached. The next element zinc has no empty inner subshell. The above is the reason why the whole gamut of *elements from scandium right up to copper is sometimes regarded as the first or iron transitional elements.*

The structure of the heavier elements is known with less degree of certainty than the lighter ones owing to multiplicity of the electrons but there is no doubt that the same fundamental principles are operative there in regulating their electronic structure.

Periodic Law and the Periodic Table —In 1869, Mendeleeff stated the Periodic Law which forms the basis for the modern classification of the elements known as the periodic table. The periodic Law may be enunciated as follows: *"The physical and chemical properties of the elements and their compounds are periodic functions of their atomic weights"* or *"if the elements are arranged in order of increasing atomic weights, their properties vary in a definite manner from member to member of the series, but return more or less nearly to the same value at certain fixed points in the series."*

The periodic table drawn up by Mendeleeff on the basis of this law contained many vacant spaces left for the still undiscovered elements, which have now been mostly filled up. The modern table based on the Mendeleeff's original one is shown in the accompanying diagram (Fig. 123). Attempts to improve upon Mendeleeff's table by quite a novel type of arrangement e.g., spiral arrangement, helix arrangement, etc., have often been made but Mendeleeff's table still stands unique as constituting a landmark in the progress of theoretical chemistry.

Description of the Periodic Table —The table contains *nine* vertical columns called groups numbered from zero to eight and a number of horizontal rows called series or 'periods'. Leaving out hydrogen which is peculiar in being the solitary member of the first series, the rest of the table can be divided

Fig. 25.—THE PERIODIC TABLE OF ELEMENTS

Period	Group 0	Group I A	Group I B	Group II A	Group II B	Group III A	Group III B	Group IV A	Group IV B	Group V A	Group V B	Group VI A	Group VI B	Group VII A	Group VII B	Group VIII
First Short Period	He 2 4·003	H 1 1·0078														
Second Short Period	Ne 10 20·18	Li 3 6·940		Be 4 9·013			B 5 10·82		C 6 12·011		N 7 14·008		O 8 16·00		F 9 19·00	
	A 18 39·94	Na 11 22·991		Mg 12 24·32			Al 13 26·98		Si 14 28·09		P 15 31·03		S 16 32·066		Cl 17 35·457	
First Long Period — First Series		K 19 39·10		Ca 20 40·08		Sc 21 44·96		Ti 22 47·90		V 23 50·95		Cr 24 52·01		Mn 25 54·94		Fe (26) Co (27) Ni (28) 55·84; 58·94; 58·69
First Long Period — Second Series	Kr 36 83·8		Cu 29 63·54		Zn 30 65·38		Ga 31 69·72		Ge 32 72·60		As 33 74·91		Se 34 78·96		Br 35 79·916	
Second Long Period — First Series		Rb 37 85·48		Sr 38 87·63		Y 39 88·92		Zr 40 91·22		Nb 41 92·91		Mo 42 95·95		Tc 43 99		Ru (44) Rh (45) Pd 46 101·7, 102·91, 106·7
Second Long Period — Second Series	Xe 54 131·3		Ag 47 107·88		Cd 48 112·41		In 49 114·8		Sn 50 118·70		Sb 51 121·76		Te 52 127·6		I 53 126·91	
Third Long Period — First Series		Cs 55 132·91		Ba 56 137·36		La etc. (rare earths) 57-71		Hf 72 178·6		Ta 73 183·95		W 74 183·92		Re 75 186·31		Os (76) Ir (77) Pt (78) 190·2, 192·2, 195·23
Third Long Period — Second Series	Rn 86 222		Au 79 197·0		Hg 80 200·61		Tl 81 204·39		Pb 82 207·21		Bi 83 209·0		Po 84 210		At 85 210 ?	
Last Incomplete Period		Fr 87 223 ?		Ra 88 226·05		Ac 89 227		Th 90 232·05		Pa 91 231		U 92 238·07				

Transuranium elements Np (93), Pu (94), Am (95), Cm (95), Bk (97), Cf (98), En (99), Fm (100), Mv (101)

Bold figures after the symbols indicate atomic numbers and figures below atomic weights

into five complete and one fractional periods, the complete periods containing 8, 8, 18, 18, and 32 elements respectively.

Hydrogen for its versatility of properties is placed alone in the first series, either in Group I with the alkali metals or sometimes in Gr. VII with the halogens. Then follow two *short periods of eight elements* which fit naturally in the eight groups from Gr. O to Gr. VII, the first period containing elements from helium to fluorine and the second from neon to chlorine. The two short periods are then followed by two *long periods of eighteen elements* each, divided into two series. The *first long period* starts with argon and ends in bromine, while the *second long period* ranges from krypton to iodine. These two long periods of eighteen elements differ from the preceding two short periods in that a group of three elements in each period—the so-called *'transitional elements'*, Fe, Co, Ni and Ru, Rh, Pd—is placed together in Gr. VIII due to the obvious difficulty of finding a suitable place for them.

The two long periods are followed by a *longer period of thirty two elements* starting from xenon and ending in the element No. 85, astatine, the lately known highest homologue of the halogens. These thirty two elements are divided into either two or four horizontal series. This *longer period* also contains a 'trio' of transitional elements (Gr. VIII), and contains fifteen very closely related elements, Lanthenum (57) to Lutetium (71), known as the *'rare earth elements.'* It might be mentioned in passing that the name 'rare earth' is a misnomer because as a group they are more abundant than say, copper, and as an individual member cerium is more abundant than many ordinary elements, say, mercury or tin.

We next reach the sixth or the last period of radioactive elements, which is only a broken period beginning from radon and stopping at the heaviest element uranium of Gr. VI. A number of elements beyond uranium have been lately synthesised by nuclear scientists and they are called *'transuranium elements'*; of them neptunium (93) and plutonium (94) are well-known through the latter's possibility of use in atomic bombs. It should be pointed out that each complete period begins with an inert gas (He, Ne, A, Kr, Xe and Rn) and ends with a halogen (Gr. VII), excepting the last period which is but incomplete.

Such a classification brings together closely related elements in one vertical group. Thus, all the inert gases fall in Gr. 0, all the alkali metals in Gr. I., the alkaline-earth metals in Gr. II, the halogens in Gr. VII and so on, the stray similarity occasionally met with among elements thus finding a thorough expression in the Mendeleeff's periodic Table.

Atomic Structure and the Periodic Table—The two most characteristic features of the periodic table are the regular variation of properties from member to member in a series and the

periodic recurrence of properties at some regular intervals. The regular variation is easily accounted for from a consideration of the atomic structures of any one period. For example, consider the structure of the elements of the first period as depicted in Fig. 121. It will be noticed that from member to member there is a regular increment of one electron in the L level. Since the outermost electrons are mainly responsible for the chemical properties of an atom, the stepwise variation of the electronic configuration of the outermost ring explains remarkably well the observed regular gradation in chemical properties.

The periodic recurrence of properties is also easily explained as being due to the recurrence of a similar arrangement of the outermost electrons. The truth of this is easily borne out by comparing the structures of any group of elements. For example, let us consider the electronic structure of the inert gases and the alkali metals collected below on the basis of the foregoing table.

Element	Atomic Number	Electron Arrangement in shell						
		K	L	M	N	O	P	Q
Noble Gases :								
He	2	2						
Ne	10	2	8					
A	18	2	8	8				
Kr	36	2	8	18	8			
Xe	54	2	8	18	18	8		
Rn	86	2	8	18	32	18	8	
Alkali Metals :								
Li	3	2	1					
Na	11	2	8	1				
K	19	2	8	8	1			
Rb	37	2	8	18	8	1		
Cs	55	2	8	18	18	8	1	
Fr	87	2	8	18	32	18	8	1

It is easily seen that all inert gas atoms have their outmost group or sub-group saturated with electrons ; and all the alkali metals are similar in structure having an one-electron-show in the outermost shell. Since only the outermost electrons are mainly responsible for the chemical properties of an element, this explains the similarity of chemical properties of elements in the same group.

Atomic Number and the Periodic Law—The existence of 'isotopes' has proved the inadequacy of atomic weights as a characteristic constant of the elements. However, the atomic number (see next section) of any element is a characteristic constant of the element and can be used as a criterion for the position of the element in the periodic table. The *periodic law* may on this basis be restated as follows: *The physical and chemical properties of the elements are periodic functions of their atomic numbers.* By arranging the elements in the periodic table on

this basis most of the serious anomalies of the table disappear or receive an able explanation with reference to its atomic structure.

Atomic Number—The term was originally applied to mean the serial number of an element in the periodic table. From the foregoing picture of the atom it may be seen that this 'roll number' of the atom is identical with its nuclear charge. Therefore, atomic number may be defined thus:—*The atomic number of any element is equal to the free positive units of electricity in the nucleus of its atom and hence, is also equal to its ordinal number in the periodic table.* Thus, hydrogen has an atomic number unity, helium 2, lithium 3, beryllium 4, and so on. Evidently, the atomic number is equal to the number of protons in the nucleus as also to the number of electrons outside the nucleus.

As described earlier, Mosley (1913) was the first to develop a method for an independent determination of atomic number of elements from their X-ray spectra. He proved that the atomic number and not the atomic weight is a fundamental constant for any element which uniquely determines its properties. The same element may exist with two or more different atomic weights (*vide* isotopes) but the atomic number in all such cases is the same. Hence, instead of atomic weights atomic number could be better utilised as a criterion of chemical properties in the periodic table. The classical anomalies in the periodic table about the positions of argon and potassium, tellurium and iodine, etc. then totally vanish and the positions of the elements follow the natural sequence of their chemical properties.

Isotopes—*Different specimens of the same element which differ in atomic mass, but are identical in all chemical properties are known as isotopes, (iso—same, topos—place).* Evidently, isotopes have the same atomic number, that is, the same nuclear charge and so occupy the same place in the periodic table.

From the standpoint of radioactivity isotopes can be classified into three kinds, *viz.*

(a) *Non-radioactive Isotopes*

(b) *Naturally radioactive isotopes.*

(c) *Artificially radioactive isotopes.*

(a) **Non-radioactive Isotopes**—The stable elements which occur in nature have been found almost always to be a mixture of isotopes and the measured atomic weight is only an average value. For example, ordinary oxygen contains three isotopes of atomic mass 16, 17 and 18 respectively. Ordinary chlorine is a mixture of two isotopes of atomic mass 35 and 37 in such a proportion that the average atomic mass is equal to the ordinary atomic weight, *viz.* 35·457. The isotopes of some typical ordinary elements with their relative abundance in nature is shown in the table below. It should be noted from the table that fluorine is composed of just one type of atom.

Atomic Number,Z	Element	Symbol	Mass number	Physical Atomic Weight, $O^{16}=16$	Relative Abundance. (per cent)
1	Hydrogen	H $_1H^2$ or D	1 2	1·00813 2·01473	99·985 0·015
3	Lithium	$_3Li^6$ $_3Li^7$	6 7	6·01686 7·01818	7·8 92·2
6	Carbon	$_6C^{12}$ $_6C^{13}$	12 13	12·00398 13·00761	98·9 1·1
8	Oxygen	$_8O^{16}$ O^{17} O^{18}	16 17 18	16·00000 17·00450 18·00369	99·76 0·04 0·20
9	Fluorine	$_9F^{19}$	19	19·00452	100·00
10	Neon	$_{10}Ne^{20}$ Ne^{21} Ne^{22}	20 21 22	19·99881 21·00018 21·99854	90·00 0·27 9·73
17	Chlorine	$_{17}Cl^{35}$ Cl^{37}	35 37	34·98·07 36·97829	75·4 24·6
82	Lead	$_{82}Pb^{204}$ Pb^{206} Pb^{207} Pb^{208}	204 206 207 208	 208·060	1·5 23·6 22·6 52·3

Though most of the isotopes present in ordinary elements are non-radioactive, there are some exceptions, the most well-known being $_{19}K^{40}$ which is radioactive and is present in very small proportion in any ordinary sample of potassium salt.

(*b*) **Naturally Radioactive Isotopes**—Isotopes were first discovered among radio-active elements. The large number of new elements whose existence was revealed by a study of radioactivity were not all distinct elements but were found to be isotopes of only a few elements. Thus, the radioelement ionium (at. wt.—230·02) obtained by the radioactive disintegration of uranium was found to have chemical properties identical with those of thorium (at. wt. 232·12). Many similar other pairs were shortly discovered and it appeared later that such elements which are chemically indistinguishable must occupy the same position in the periodic table, since though they may differ in atomic mass, their atomic numbers are the same (Fig. 116). A simple consideration of the radioactive disintegration series shows that even the nonradioactive element lead obtained as the final product of the uranium disintegration series (Fig. 115) must have an atomic weight different from ordinary lead. For, by passing from uranium (at. wt.—238·2) to lead, 8 alpha particles, each of mass 4, are expelled and hence the resulting lead should be of mass 206·2, as contrasted with ordinary lead which has an atomic weight

of 207·2. This is actually the case as lead obtained from uranium minerals has been found to have an atomic weight of 206·05, a value as high as 0·5 per cent lower than that of ord.nary lead.

(c) **Artificially Radioactive Isotopes**.—With the development of atomic piles as also machines such as cyclotron, betatron, etc. to produce high-energy missiles to bombard atomic nuclei, a few hundred radioactive isotopes of ordinary elements have been produced. These have been already discussed in some details (P. 375) and their extensive application as 'tracers' has been indicated.

Since protons and neutrons have unit mass and the mass of electrons is negligible, all isotopes should have whole number values for their atomic weights. The fractional atomic weights of ordinary samples are due to their being a mixture of isotopes present in some invariable ratio unchanged by any chemical process. The mass of a single isotope however is not an exact whole number owing to matter-energy interconversion.

Atomic Structure of Isotopes.— Since atomic number unequivocally characterises an element, it is evident, that the isotopes of the same element have the same atomic number i.e. the same nuclear charge. As the nuclear charge is wholly contributed by the protons, all the isotopes of the same element have the same number of protons in the nucleus and they differ only in the number of neutrons in the nucleus. Obviously, the extranuclear structure for all isotopes of the same element is identical. The following structures for the three known isotopes of oxygen (atomic number, 8) of mass 16, 17 and 18 respectively illustrate this.

Nucleus	Outside
Oxygen (16) :—8 protons+8 neutrons.	2 ; 6 = 8 electrons.
Oxygen (17) :—8 protons+9 neutrons.	2 ; 6 = 8 electrons.
Oxygen (18) :—8 protons+10 neutrons.	2 ; 6 = 8 electrons.

Separation of Isotopes.—Since isotopes of the same element have nearly the same chemical and physical properties, all methods of their separation have to be necessarily based on this slight difference in properties. Evidently, the efficiency of any such method would be quite low. The efficiency is generally increased by utilising a large number of stages, called *cascade principle*, such that the output of one stage is automatically made the input of the next stage in a large number of succession of stages sometimes well over a few thousand. In principle this is similar to the separation of two very closely boiling liquids by fractional distillation.

The most notable examples of separation of isotopes in large scale are (i) the separation of U^{235} from ordinary uranium which contains about three quarter per cent of this isotope; this was needed for the manufacture of atom bomb and also for some kind of atomic reactors; and (ii) the separation of heavy water and so heavy hydrogen from ordinary water.

The methods in general use are as follows :

(a) *Gaseous diffusion method*—Since isotopes differ in mass, they would also differ in their rate of diffusion as given by Graham's law of diffusion.

This almost insignificant difference is intensified by the cascade principle and in this way uranium has been separated on a large scale into its isotopes, U^{235} and U^{238} by utilising the fractional diffusion of UF_6 vapour.

(b) *Thermal diffsion method*—The method depends on the principle that if a steady temperature gradient is maintained inside a fluid, the lighter atoms tends to concentrate from the colder to the warmer region. This principle has been utilised to develop techniques by which virtually complete separation of ordinary chlorine into its two isotopes, Cl^{35} and Cl^{37} was achieved.

(c) *Mas Spectrograph method*—Since mass spectograph separates the isotopes, a suitable device for collecting the isotopes would effect the required separation.

(d) *Fractional Electrolysis method*—Striking results had been obtained by Washburn and Urey (1932) who applied electrolytic method for the separation of the isotope of hydrogen of mss 2, called heavy hydrogen or deuterium (symbol D), which occurs in ordinary water to the extent of about 0·02 per cent. The atomic structure of heavy hydrogen is the same as that of ordinary hydrogen except that its nucleus contains a neutron along with the proton to give the extra mass. Water containing heavy hydrogen is known as heavy water (D_2O) as it is about ten per cent heavier than ordinary water and also differs from it in many physical constants (*e.g.* melting point, 3·8°C; B.P., 101·4°C; etc.). There is also a radioactive isotope of hydrogen of mass 3, called tritium (half life about 12 years), which is produced by artificial means.

The usual method of preparation of heavy water is to electrolyse a 0·5 molar solution of sodium hydroxide using nickel or nickel and iron electrodes until the volume is reduced to about ten per cent of the original. The concentrated electrolyte so produced is neutralised with carbon dioxide and distilled, and the distillate is electrolysed after addition of some undistilled concentrated electrolyte to bring the concentration to 0·5 N sodium hydroxide. By repetition of the process seven times, water containing 99·0 per cent D_2O is obtained.

(e) *Isotope Exchange method*—All the foregoing methods depend on difference in physical properties, but this method depends on the slight difference in chemical properties between the isotopes. This method after utilising the usual cascade principle has been developed into quite efficient methods for enrichment and separation of various isotopes.

Exercises

1. Write down the electronic structure of the following atoms :— (*i*) Potassium, (*ii*) Calcium, (*iii*) Aluminium, (*iv*) Silicon, (*v*) Arsenic and (*vi*) Astatine.

2. Write an essay on the relationship between electronic structure and position of an element in the Periodic table.

3. Discuss the electronic structure of the elements in the first long period of the periodic table.

4. Name the three isotopes of hydrogen and discuss how they are obtained and also their structure.

5. Discuss the significance of the fact that samples of lead obtained from different sources have different atomic weights.

6. If no isotopes were existing, what difference would this fact make to our table of atomic weights.

ELECTRONIC THEORY OF VALENCY

Valency : Historical Introduction—*Earlier ideas of chemical union*: The nature of chemical union has been much speculated upon. *Dalton* was of opinion that the forces responsible for chemical union were perhaps of gravitational nature, while *Davy* from his researches on electrolysis was led to the conclusion that chemical combination was electrical in nature. Similar idea was elaborated by *Berzelius* in 1807, in his once-celebrated '*Dualistic Theory*'. After the fall of the dualistic theory, the '*theory of types*' of Dumas held the sway for a few years where all chemical compounds were made to conform to certain plans of atomic arrangement called 'types' such as water type, ammonia type, etc.

Growth of the Idea of Valency—The idea that atoms have fixed combining capacity was reached by *Frankland* in 1852, from a study of organo-metallic compounds. The idea was gradually adopted by other chemists, and valency or saturation capacity was defined as the number of hydrogen atoms with which one atom of a given element could combine. *Kekule* adopted the idea that the valency of a given element was fixed in number ; he assigned tetravalency to the carbon atom and explained the structure of organic compounds as due to a mutual saturation of their combining capacities.

Spatial Disposition of Valency—A notable advance on our knowledge was made by *van't Hoff* and *Le Bel* (1874) who propounded that the combining capacity of atoms was a force acting with definite units of affinity in fixed direction and particularly, the four valencies of a carbon atom were directed towards the angular points of a regular tetrahedron. This idea of fixed spatial distribution of valency was also embraced by *Werner* in 1891 in his celebrated theory of the structure of the complex inorganic compounds.

The theory of valency could not grow further until a suitable picture of the atom was developed. With the discovery of electrons and the development of our ideas on the electronic structure of the atom, it became possible to depict chemical combinations in terms of the ultimate units of matter and thus arose the electronic theory of valency.

Origin of the Electronic Theory of Valency—The electronic theory of valency was originated by Kossel (1916) and Lewis (1916) and was amplified by Langmuir (1919). It is evident that the type of valency which brings about the union of sodium with chlorine is certainly not the same as can unite chlorine atoms to carbon, for, the compound sodium chloride formed in the first case is a crystalline, high-melting solid which dissolves in water

forming ions, whereas the second compound carbon tetrachloride is a liquid and a typical nonelectrolyte. The former type of valency which brings about the union between a strongly electropositive and a strongly electronegative atom giving rise to an electrolyte is called *heteropolar valency* or *electro-valency*. The other type of valency which unites two atoms of the same type, (for example, two electronegative atoms forming a non-electrolyte) is called *homopolar valency* or *co-valency*.

Electrovalency or Ionic Bond—The stablest configuration of electrons is possessed by the inert gases as they have their outermost shell or subshell saturated. Taking for example He (2), Ne (2,8) and Ar (2,8,8) we find that all of them have their outermost shell or subshell saturated. Any element which has got less than this number of electrons in the outermost shell, tends to pass to the nearest inert gas configuration (*i.e.* saturated outermost shell) either by taking electrons or by giving up electrons.

The sodium atom has got its K shell and L shell filled up and has got only one electron in the outermost M shell. Thus sodium appears to have one electron in excess of the nearest inert gas and so it may easily give up this electron to pass into the nearest inert gas (neon) configuration. Since the atom is as a whole neutral this *donation of electron* will leave the sodium atom with unit positive charge *i.e.*, Na^+ ion. A chlorine atom (2,8,7) on the other hand, has got 7 electrons in the outermost shell and it may take up this single electron from a sodium atom to fill up its outermost shell to assume the electronic configuration of the nearest inert gas, krypton. It will thus form negatively charged chlorine atom *i.e.* chlorine ion.

As a result of the electrostatic attraction between opposite charges, the sodium ion and the chlorine ion will be held tight in the crystal lattice of sodium chloride and would form sodium chloride crystals. Since there are as many Na^+ ions as Cl^- ions in any macroscopic crystal of sodium chloride we are justified to write its formula as $Na^+ Cl^-$, without meaning that the molecule $Na^+ Cl^-$ exists as such in the crystal. In fact, in the sodium chloride crystal each sodium ion is equally attracted along three

Na   Cl   Na⁺   Cl⁻
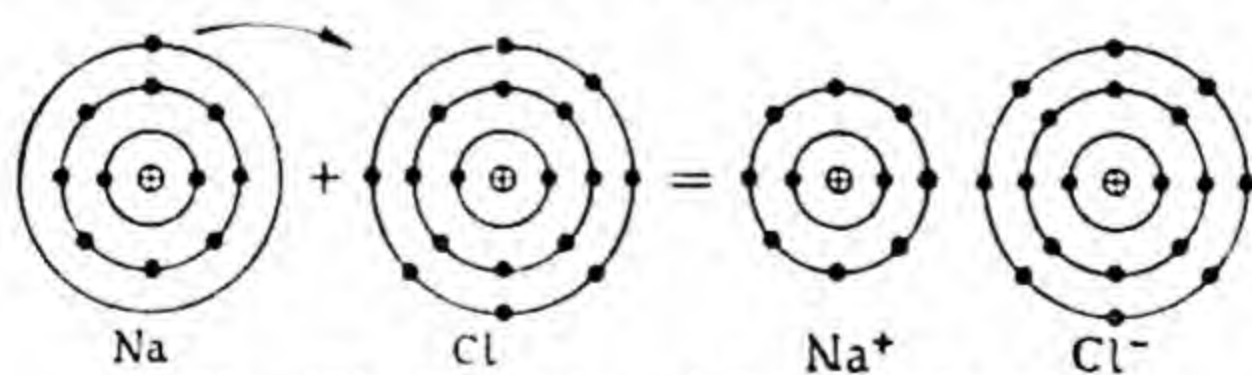
Fig. 124—Formation of Sodium Chloride

mutually perpendicular lines by six chlorine ions and *vice versa*. Such strong well-balanced electrical attraction symmetrically distributed on all sides gives the crystal a high melting point and density (*vide* p. 76).

The electron transfer may be represented as shown in Fig. 124.

The ease with which the sodium atom loses an electron is reflected by its low ionisation energy and low electron affinity, whereas the electron affinity of chlorine atom which is a measure of its tendency to capture electrons is relatively high as also its ionisation energy. The monovalency of sodium and the alkali metals which have got electronic structure similar to sodium and similarly, the monovalency of the halogens which have electronic structure in the outermost shell same as chlorine are thus easily accounted for.

The elements magnesium, calcium, etc. (Gr. II) have two electrons in the outermost shell which they can donate to negative elements having unsaturated outermost shell, thereby themselves passing to the nearest noble gas structure, and therefore they are bipositive in valence. The outermost electrons which are thus solely responsible for the valency of an element are called *valency electrons*. Electrovalency is operating in all compounds which are electrolytes and further examples are shown below.
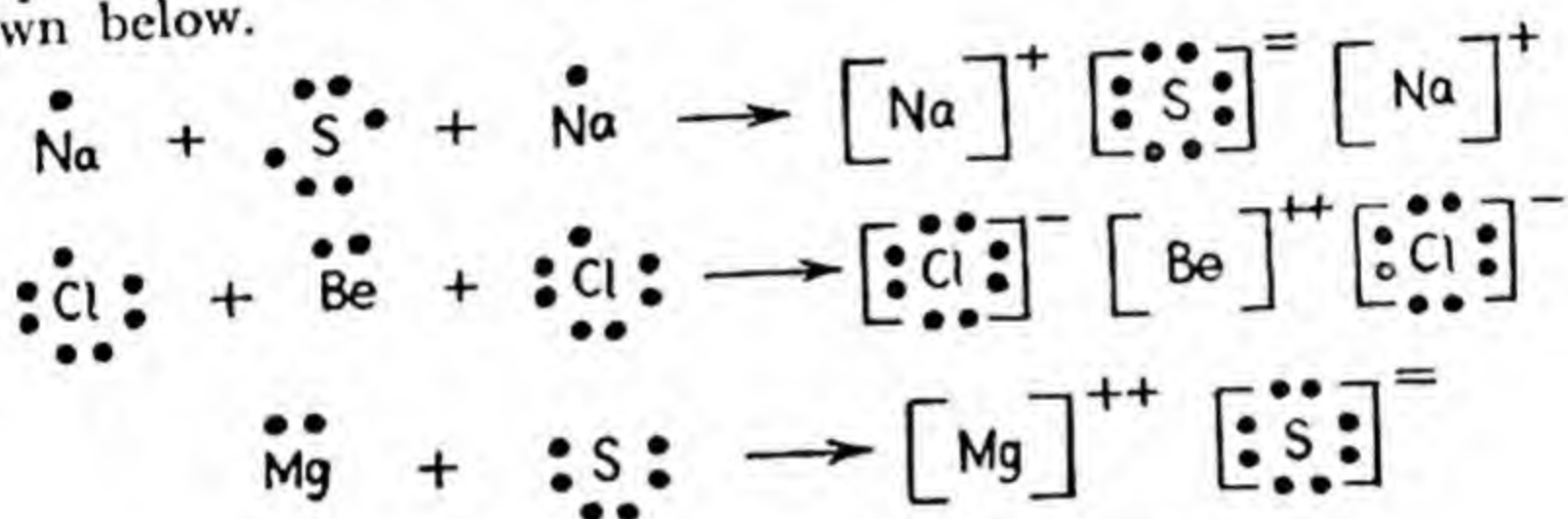
Fig. 125—Examples of Electrovalency

High Values of Electrovalency —Loss or gain of electrons by atoms becomes increasingly difficult with successive electrons as each loss or gain of electron produces unit charge. Evidently, the effect of the nuclear positive charge is such that the lower the size of the atom, the more difficult it is to form positive ions, and conversely for negative ions. This explains why in the first short period, the first two atoms, Li and Be show positive electrovalency of one and two respectively, but boron is not electrovalent at all. For the same reason in the second short period where the corresponding atoms are a little bigger, the first three elements, Na, Mg and Al form simple ions, but no tetrapositive silicon ion is known.

For similar reasons, hardly ever a simple negative ion with more than two units of charge is met with. However, the effect of size will necessarily be in the reverse direction to that of the positive ions, and so, smaller negative ions will be stabler than bigger ones. This is the reason why fluorine readily forms F^- ion, oxygen form O^{--} ion with difficulty and nitrogen does not form tri-positive ion at all.

Ions without Inert-Gas Structure -Though most ions as explained in the previous para have the electronic structure of a noble gas, there are a large number of ions, all cations, with other structure. For example, referring to the table on P. 384 it would be found that none of the bipositive or high-valent ions formed by the elements from scandium to copper has the inert gas structure. Thus the stable Cr^{+++} ion has its outermost $3d$ shell occupied with only 3 electrons. Evidently some other forces are operative about which little is known at present which determine the stability and the variability of valency of these ions.

Covalency : Shared Electron-Pair Bond—G. N. Lewis (1916) is the originator of the idea of the covalent bond ; this type of bond is so widely operative in chemical combination that he called this *'the chemical bond'*. In fact, barring electrolytes and inter-metallic compounds all other chemical compounds owe their existence to this type of bond.

It is evident that electrovalency can operate only in compounds like NaF where the union is between two atoms of opposite types. But the large majority of compounds formed by the union of similar atoms and showing hardly any sign of ionisation, can not be ascribable to electrovalency and some other type of mechanism must be at play in such compounds. For example, a fluorine atom combines with another fluorine atom to form a molecule of F_2 and this certainly can not take place by simultaneous loss and gain of electron as in electrovalency.

Lewis however solved this enigma by pointing out that atoms can pass to the nearest stable electronic configuration (*i.e.* electronic configuration of the nearest inert gas) not only by transfer of electrons as described in the previous section but also by sharing of electron pair.

For example, if there are two chlorine atoms and supposing that both of them try to fill up their octer to assume the argon structure, it is impossible to do this by donation of electrons since each of the two atoms contains only seven valency electrons each. But this is easily realised if they have two electrons in common (see Fig. below), one of which is contributed by each atom ; this *sharing of a pair of electrons* would make each atom finding itself surrounded by an outermost ring of eight electrons though there are in all fourteen electrons.

$$: \overset{..}{\underset{..}{Cl}} \cdot \qquad + \qquad \cdot \overset{..}{\underset{..}{Cl}} : \longrightarrow \; : \overset{..}{\underset{..}{Cl}} : \overset{..}{\underset{..}{Cl}} :$$

Chlorine	*Chlorine*	*Chlorine*
atom	*atom*	*molecule*

$$: \overset{\cdot}{\underset{\cdot}{N}} \cdot \qquad \qquad \cdot \overset{\cdot}{N} : \longrightarrow \; : N : : : N :$$

Nitrogen	*Nitrogen*	*Nitrogen*
atom	*atom*	*molecule*
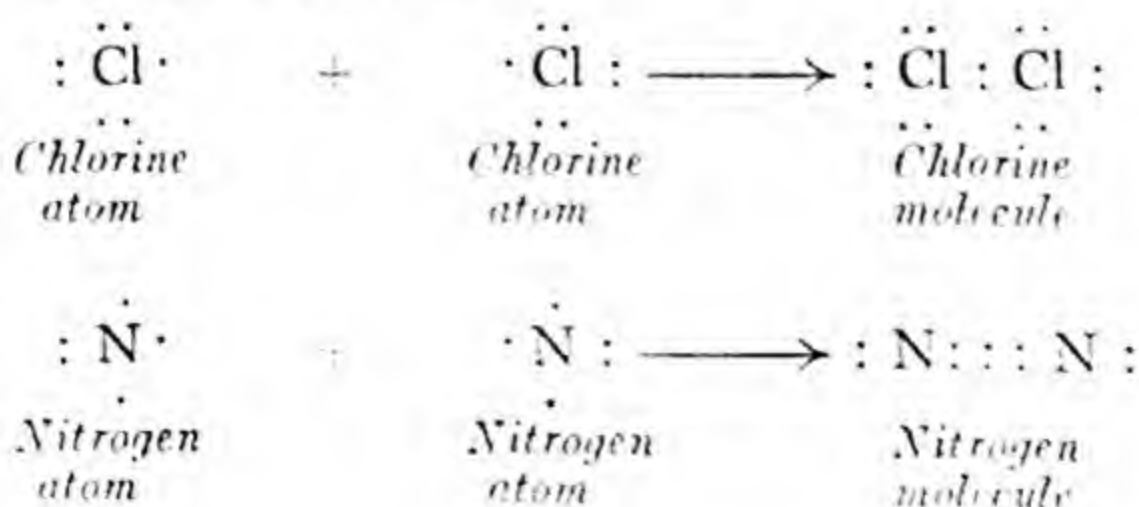
This shared electron pair is the *covalent bond* and this type of bonding caused by sharing of electron pairs is called *covalency*. This tendency of most atoms to get surrounded by a complete outermost shell of eight electrons is often referred to as the *octet theory of valency*. Compounds formed by the exercise of covalency are non-ionising in solution since considerable force would be required to disrupt the atoms. A nitrogen atom has got only five outermost electrons and so two nitrogen atoms can combine to form the N_2 molecule by sharing six electrons (see Fig. above). Since each pair of electrons is equivalent to a conventional chemical bond, these six common electrons stand for a triple bond.

Covalency is operating in organic compounds and also in a number of inorganic compounds. Some very simple but instructive cases of pure co-valency are shown below diagrammatically—

H H : C̈ : H Ḧ	H H C̈ : : C̈ Ḧ Ḧ	: C̈l : : C̈l : C̈ : C̈ : : C̈l :	H H : N̈ : H
Methane	*Ethylene*	*Carbon tetrachloride*	*Ammonia*
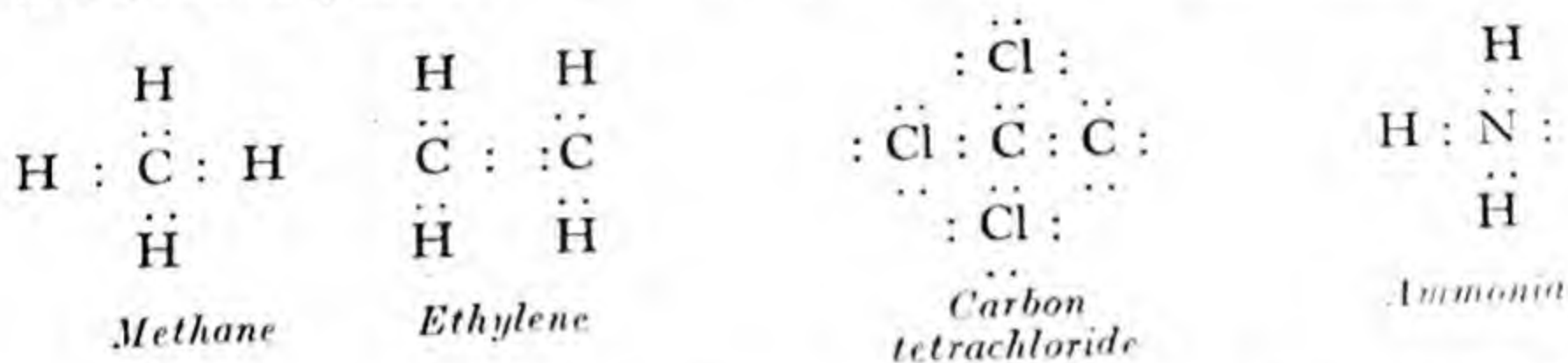
In methane the carbon atom has got its outer ring saturated with 8 electrons by sharing 4 pairs of electrons with hydrogen atoms. Each of the latter has not only two electrons to share but these are quite sufficient to saturate its outermost K-shell to give it the electronic configuration of helium. It is to be noted that the sharing of electrons occurs in pairs and each pair of electrons is equivalent to a conventional chemical bond. Hence, double bond is to be represented by the sharing of four electrons as shown in ethylene and a triple bond by the sharing of six electrons *i.e.* three duplets as shown in the nitrogen molecule (*see* diagram). In fact, Lewis was led to his theory of co-valency by the remarkable fact that excepting three or four cases, such as NO, NO_2, ClO_2, etc. all known chemical compounds contain an even number of electrons.

We have written down in the next page a few more electronic structures, where for convenience we have replaced the electron pair by the conventional line. We have intentionally represented water as

H
|
H — O :   instead of H — Ö — H to bring home the

fact that the two valencies are directed more near to a right angle (to be more precise about 110°) than to a straight angle. It would be very instructive if the student writes down the electronic formulæ for a number of common compounds.

Covalent compounds. (*Arrow represents co-ordinate covalency*).
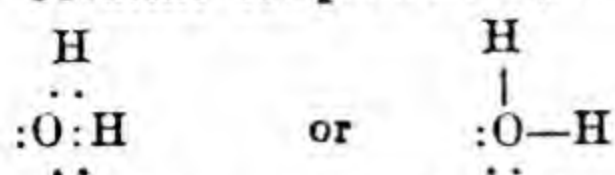
```
  H                   H                        ..
  ..                  |                       :S—Cl:
:O:H      or        :O—H                       |   ..
  ..                  ..                      :Cl:
                                               ..
```
Water (Triangular molecule)   Sulphur Dichloride

```
  ..                :C≡):                    ..        ..
{ :O—H }            :C=O:                   :O::C::O:
  ..               Carbon Monoxide          Carbon dioxide (*linear*)
```
Hydroxyl Ion
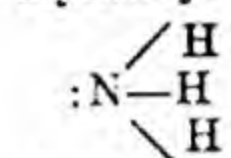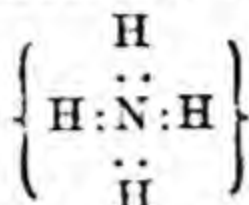
```
    /H                   H      +            ..
:N—H              { H:N:H }                 :Cl:
    \H                   ..                   |    ..
Ammonia (*pyramidal*)    H                  :P—Cl:
              Ammonium Ion (tetrahedron)     |    ..
                                            :Cl:
                                             ..
                                         Phosphorus trichloride
```
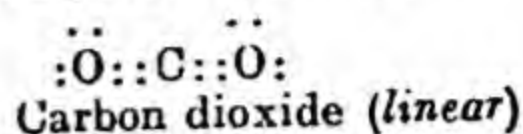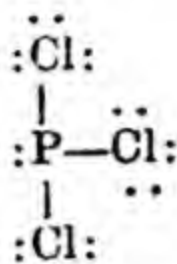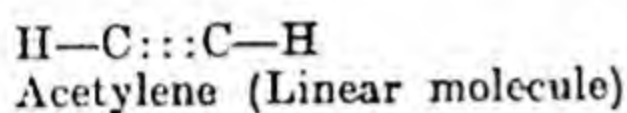
```
                                             ..
H—C:::C—H                                    :O—H
Acetylene (Linear molecule)                   |   ..
                                              B—O:
                                              |   |
H—C:::N :                                    H—O : H
Hydrogen cyanide                              ..
(Linear molecule)                           Boric Acid
```
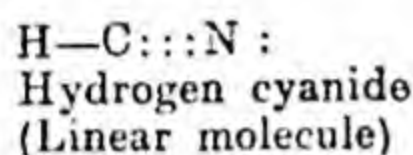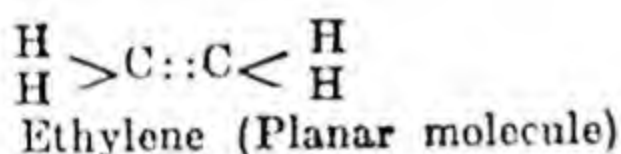
```
H        H                                   ..
 >C::C<                                      H : O—H
H        H                                    |    |   ..
Ethylene (Planar molecule)                  :O—Si—O:
                                             ..   |   |
H                                            H—O : H
|                                             ..
:S—H                                      Orthosilicic Acid
 ..
Hydrogen Sulphide
 ..                                          ..
:O:                                         :O—H
 ↑   ..                                      |    ..
:Cl—O:                                      :S—O:
 ↓   ..                                      ↓    |
 H                                               H
:O:                                          :O:
 ..                                           ..
(Chloric Acid)                           (Sulphurous Acid)
```
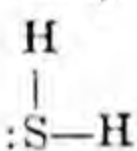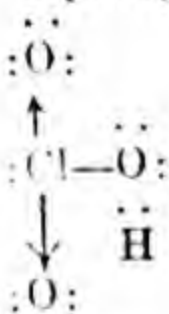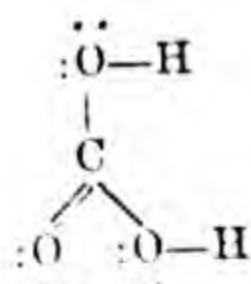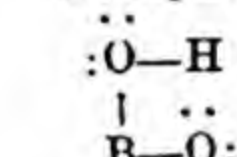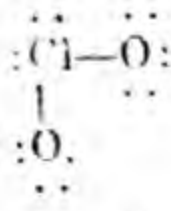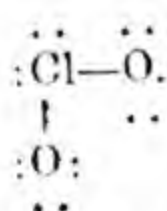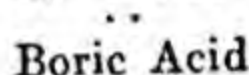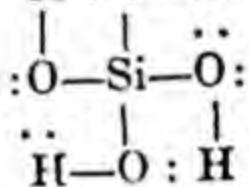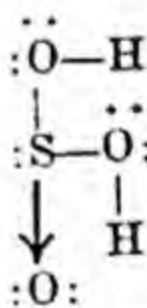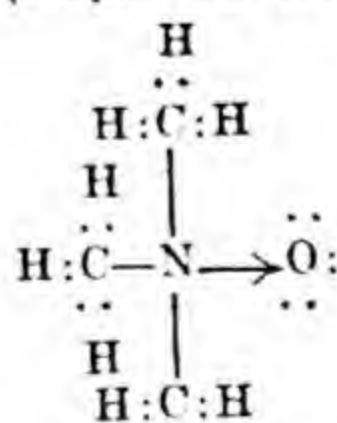
```
                                                 H
  ..                                             ..
 :O—H                                         H:C:H
  |                                           H  |
  C                                            .. |    ..
 /‖\                                          H:C—N→O:
:O  :O—H                                      .. |    ..
 ..   ..                                      H  |
(Carbonic Acid)                               H:C:H
                                              ..
                                               H
                                        (Trimethylamine oxide)
```

```
 ..   ..          ..  ..              ..  ..
:Cl—O.          :Cl—O:              .Cl—O :
 |   ..           |   ..              |   ..
:O:             :O.                 :O:
 ..               ..                  ..
```
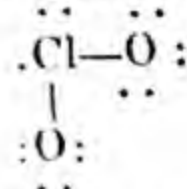
(The molecule of chlorine dioxide containing an odd number of electrons in all three possible forms, called by the general term, resonance forms, is shown. The actual molecule is a *resonance hybrid* of the three forms *vide* P. 402).

Shape of Molecules —We have already seen that the electrons in an atom are said to be in orbitals which are designated as s, p, d, f, etc. (*vide* Table on P. 384). The s orbital can accommodate only one pair of electrons (*i.e.* two electrons of opposite spin) whereas the p-orbital can accommodate three such pairs. However, the s-orbital is spherically symmetrical round the nucleus like the skin of an orange, and so it is non-directional so far as an approaching atom is concerned. The p-orbitals however are shaped like three dumb-bells at right angles to one another. Hence, p-orbitals prefer certain direction in space and so molecules formed by the exercise of p-orbitals have non-linear geometrical shapes. Thus, the water molecule is V-shaped whereas ammonia is pyramidal. The shape of many inorganic complexes are explained on such basis.

The Nature and polarity of the covalent Bond —Though we have so far described the electron as a particle it would be more in keeping with reality if each electron rotating in an orbit is conceived of as a cloud of negative charge round the nucleus the maximum concentration of the electron cloud being on the orbit. The electron pair bond may then be looked upon as a concentration or overlapping of a major portion of the two electron clouds. This concentration of electronic charge keeps the two positively charged nuclei together and stands for the conventional chemical bond. This 'smearing' out' of the electron round the nucleus is a necessary consequence of the quantum mechanical representation of the atom and arises out of the uncertainty about the exact location of the electron.

The electron pair representing the chemical bond should not however be regarded to be equally shared between the two bonding atoms. In a bond of the H : Cl or C : Cl type, chlorine being more electronegative or electron-attracting, the electron pair is closer to or under stronger influence of the chlorine atom. Hence, the H—Cl or C—Cl bond becomes polar, the chlorine end becoming the negative end of the dipole. This explains the origin of dipole moment (P. 88) of all covalent compounds.

Difficulties of the Octet Theory of Covalency —The Octet theory is not without its difficulties. Of these we might mention the following three types of behaviour not in strict conformity with the octet theory, *e.g.* (a) molecules with odd number of electrons, (b) atoms with less than eight electrons in the outermost valency shell and (c) atoms with more than eight electrons.

(a) *Odd-electron molecules*—As already pointed out Lewis was led to the theory of shared electron pair bond from the remarkable fact that of the thousands of known compounds, only a very few, for example, NO, NO_2, ClO_2 and just a very few more, contain an odd number of electrons. All these compounds are however rather unusual in the sense that they are extremely reactive, are highly colored and are paramagnetic. Stabilisation

by resonance (*see* later) certainly plays a part in their occurrence in the free state (*vide* the structures of ClO_2 on P. 398).

(b) *Atoms with Incomplete Shells*—For reasons already explained (see P. 396) the compound BF_3 is not electrovalent, and so it is covalent. The boron atom however has here, as in many other boron compounds, only an incomplete shell of six electrons in the outermost shell. Such compounds are however highly active and behave as electron acceptors (P. 401), though their structure is none too clear.

(c) *Atoms with expanded Valency Shell*—There are many well-known compounds, viz., PCl_5, SF_6, OsO_8, etc., which must be conceded ten, twelve and sixteen electrons respectively in the outermost shell. Similar violation of octet rule is observed in the case of many iodine compounds, *e.g.* iodine penta- and hepta-fluoride (IF_5, IF_7), tri-iodide ion ($I_3{}^-$), etc. Such behaviour is also common among heavier metals whose outermost shell is known to be theoretically capable of accommodating many electrons. It is gratifying however to note that no such expansion of shell takes place with the elements of the first short period in accordance with theory which sets their maximum capacity to be 8 electrons in the valency shell.

Co-ordinate Covalency—There is another type of co-valency called co-ordinate covalency or semipolar bond or sometimes dative bond in which the common pair of electrons is supplied by one of the two atoms held together; this type of valency usually exists in complex compounds. The sulphate ion, $[SO_4{}^{--}]$ is an illustrative example, where the oxygen atoms are held to the central sulphur ion by this type of valency.

$$
\overset{\cdot\cdot}{\underset{\cdot\cdot}{:S:}} \;+\; 4\,\overset{\cdot\cdot}{\underset{\cdot\cdot}{:O}} \qquad\longrightarrow\qquad
\begin{array}{c}
\overset{\cdot\cdot}{:O:} \\[2pt]
:O:S:O: \\[2pt]
:O: \\[-2pt]
\end{array}
$$

S^{--} *ion*   *Oxygen atom* $SO_4{}^{--}$ *ion*
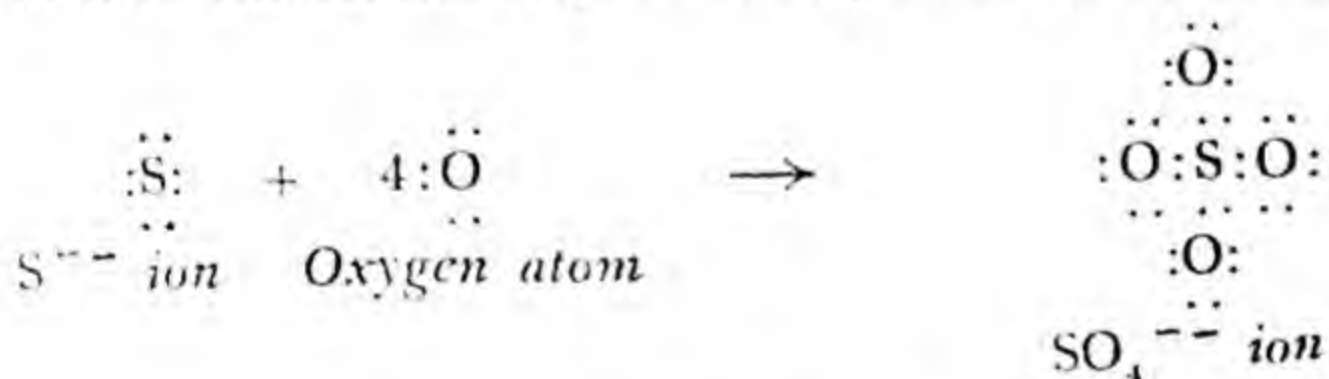
Some more examples are shown in the case of a few oxyacids on P. 398 where semipolar bond has been indicated by arrow instead of the conventional line signifying that both the electrons have been contributed by one of the atoms. As far as the strength of the bond is concerned it makes no difference whether the bonding electron pair has been supplied by both the atoms or by one of the atoms and so co-ordinate covalency is as good as covalency and there is no necessity to distinguish the two, except for specific purpose.

Another illustrative example of co-ordinate covalency is supplied by the combination of trivalent boron compounds which have only six electrons in the outermost shell of boron, with compounds like NH_3, PCl_3, etc. which contain a lone pair of

electrons, to give molecular compounds like $BF_3 - NH_3$, $BCl_3 - PCl_3$, etc. as shown below:—

$$
\begin{array}{ccc}
Cl & Cl & Cl\ Cl \\
Cl:\overset{\cdot\cdot}{P}: \ + \ \overset{\cdot\cdot}{B}:Cl \ = \ Cl:\overset{\cdot\cdot}{P}:\overset{\cdot\cdot}{B}:Cl \\
Cl & Cl & Cl\ Cl
\end{array}
$$
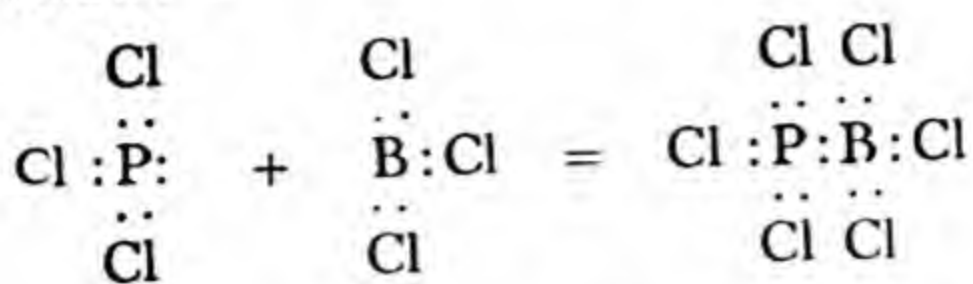
Resonance—Very often the same compound can be represented by a number of alternative electronic structures. In such cases the actual behaviour of the molecule is a composite of all the alternative structures. Here, the molecule is said to be a *resonance hybrid* of the possible structures and the molecule is said to have *resonance* between the two or more electronic structures. The importance of resonance comes from the fact that molecules possessing resonance are found by quantum mechanical calculations to possess an extra degree of stability, and the more equivalent are the resonating structures, the more stable is the actual molecule.

Thus, ozone can be represented by two resonating forms. These are

$$
\begin{array}{cc}
\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{O}: & \overset{\cdot\cdot}{O}-\overset{\cdot\cdot}{O}: \\
| & \| \\
:\overset{\cdot\cdot}{O}: & :O
\end{array}
$$

These two forms are equivalent and this gives an additional degree of stabilization to the molecule which is one of the factors contributing to the stability of this unusual molecule. Also, resonance not only gives stability to the molecule but also makes the two O—O bonds in ozone equivalent, each bond having the characteristics of a single as well as a double bond.

The student should carefully note that ozone does not contain a mixture of the above two types of molecules in equilibrium but contains only one type of molecule whose behaviour can be approximated by a combination of the two forms together with an added degree of stability. A similie, though deceptive like all similies if pushed too far, may help to clarify understanding. A green glass plate, when viewed through, looks exactly the same as a combination of a yellow and a blue glass plate and so, we may say that the green is equivalent to a combination of blue and yellow, just as the actual molecule is a combination of the contributory resonating forms.

Resonance is very common among organic molecules, a simple example being the equivalence of the two oxygen atoms of the $-COO^-$ ion. Some more examples are shown below. For CO_2 it may be noted that the first two forms being equivalent are more important than the third form.

$$:\ddot{O}-C\equiv O:\qquad :O\equiv C-\ddot{O}:\qquad :\ddot{O}=C=\ddot{O}:\qquad\qquad CO_2$$

$$:\ddot{S}-C\equiv\ddot{S}\qquad \ddot{S}\equiv C-\ddot{S}:\qquad\qquad\qquad\qquad CS_2$$

$$:\ddot{N}=N=\ddot{O}:\qquad \ddot{N}\equiv N-\ddot{O}:\qquad\qquad\qquad\qquad N_2O$$

$$:\ddot{N}=C=\ddot{O}:\qquad \ddot{N}\equiv C-\ddot{O}:\qquad :\ddot{N}-C\equiv\ddot{O}\qquad CNO^-$$

$$:\ddot{O}-S=\ddot{O}:\qquad :\ddot{O}=S-\ddot{O}:\qquad\qquad\qquad\qquad SO_2$$
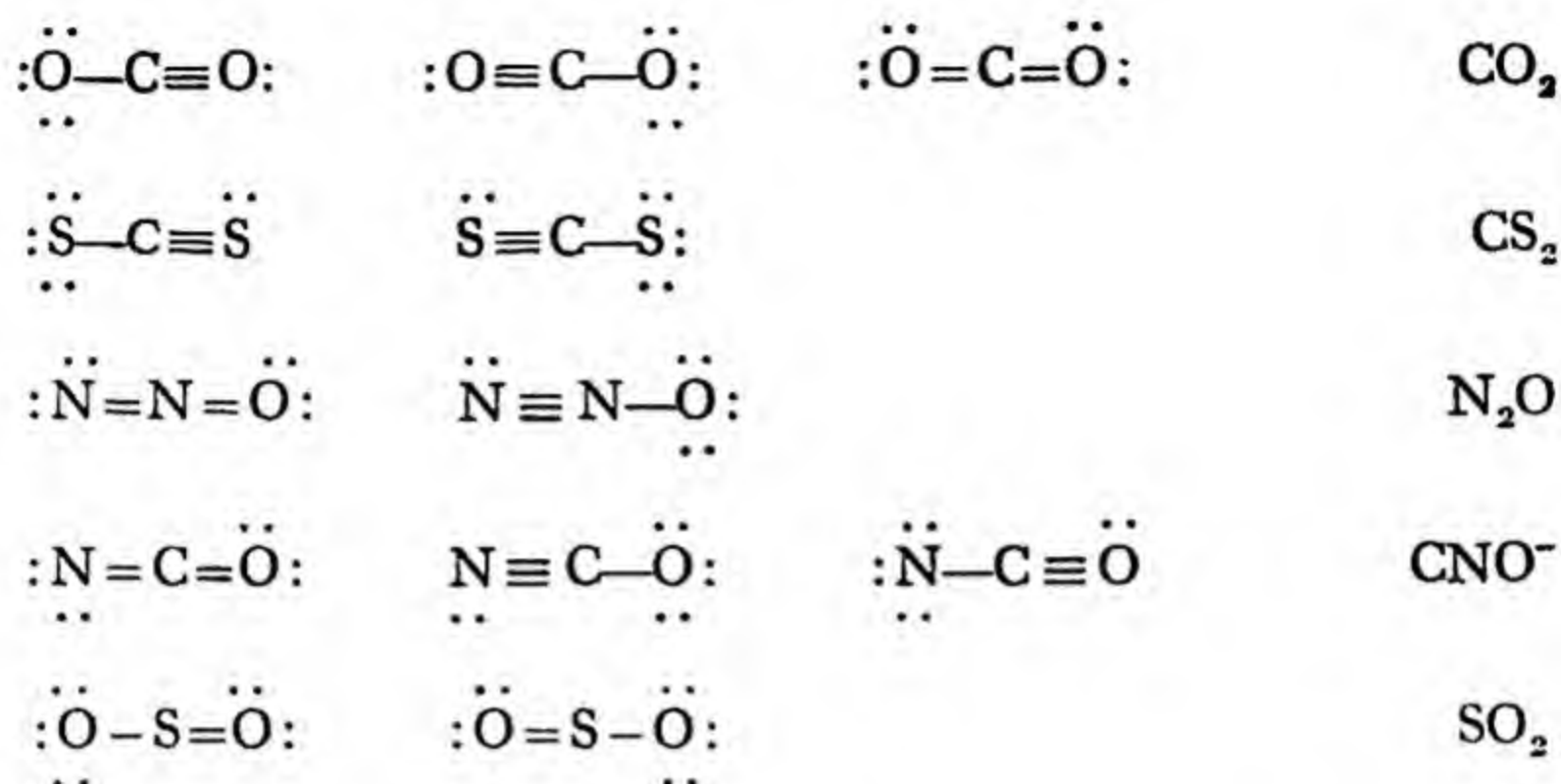
The theory of resonance is now widely used by organic chemists and has been quite successful in explaining varied facts.

Hydrogen Bond—The hydrogen atom though traditionally monovalent shows a variety of phenomena which indicate that in some compounds its behaviour is in effect that of a bivalent atom. The earliest of such idea was advanced to explain the weak basic nature of ammonium hydroxide in contrast to the quaternary ammonium hydroxides. Thus NH_3 combines with a water molecule to form the covalent compound NH_4OH, which is only very sparingly ionised.

$$NH_3 + H_2O \longrightarrow H_3N..HOH \rightleftharpoons [NH_4]^+ + OH^-$$
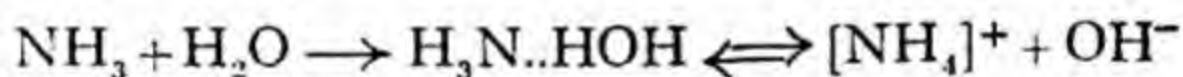
In the compound $H_3N...HOH$, one of the hydrogen atoms is behaving like a bicovalent atom, a bridge between the oxygen and the nitrogen atoms. In quaternary ammonium hydroxides, say, $N(CH_3)_4OH$ no such bridge formation is possible and so the latter are strongly ionised and behave as bases practically as strong as caustic soda.

Such hydrogen bond is responsible for the association of HF, H_2O, alcohols, etc., as shown below, ice being wholly of structure (ii). Dimerisation of acetic acid (iii) or other fatty acids is also ascribed to such hydrogen bonding. Many unusual facts of organic chemistry, particularly the special physical properties of ortho- compounds are easily explained on this basis. For examp'e, o nitro phenol and salicylaldehyde are easily volatile in steam whereas the para-isomers are not, and this is easily explained by virtual six-membered ring formation through hydrogen bond.

(i) H – F...H – F...   (ii) ...Ö – H...Ö – H...

(iii) $CH_3C\begin{matrix}O...H-O\\ \diagdown\diagup\\ O-H...O\end{matrix}C.CH_3$

(iv) *O-nitrophenol,*

(v) *Salicylaldehyde*
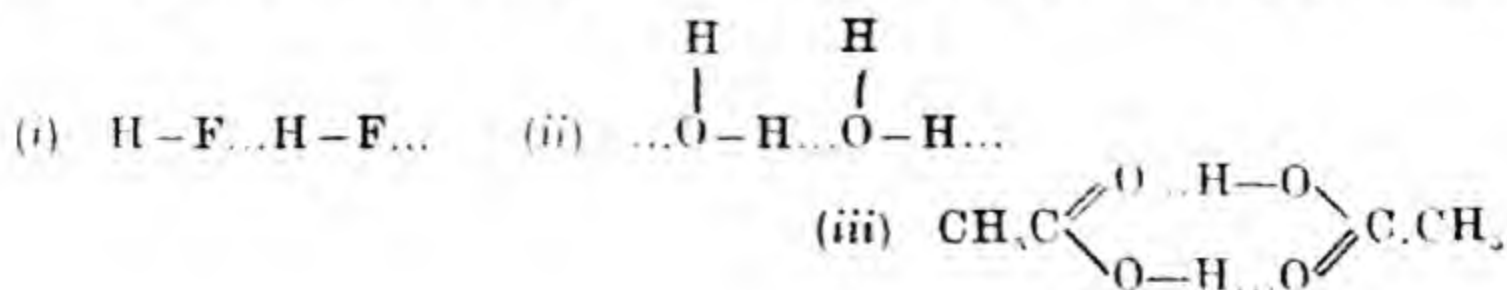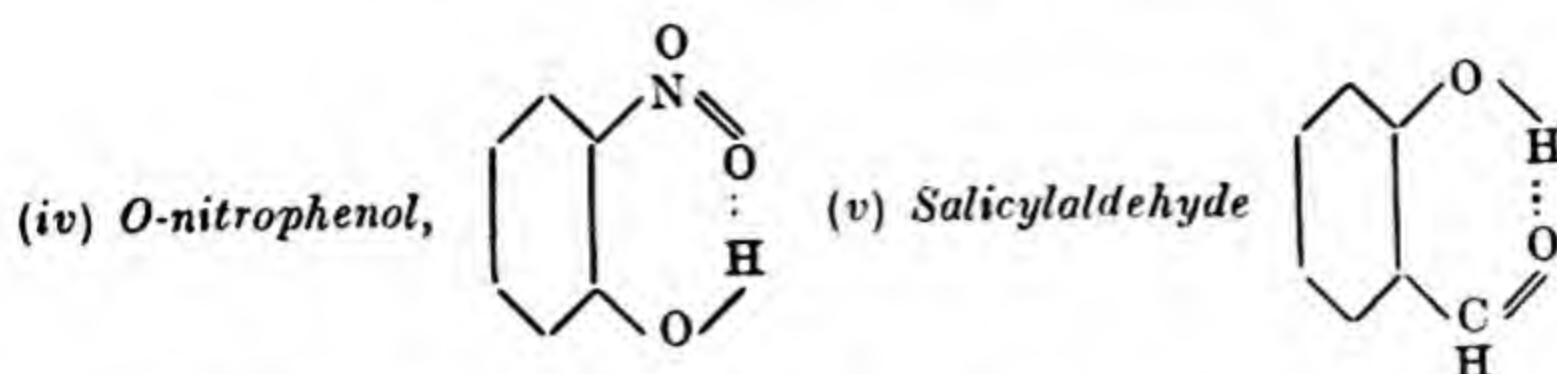
It is to be noted that hydrogen bond is operative only for bonding highly electronegative atoms, viz., F,O,N and sometimes Cl. The explanation that the hydrogen bond $A-H-B$ is a resonance hybrid of $A...H-B$ and $A-H...B$ is not acceptable because the hydrogen atom is hardly ever midway between the two atoms; neither is a truly bicovalent explanation acceptable on theoretical grounds. It is generally believed that the mechanism of hydrogen bond is electrostatic in origin, the bare proton owing to its positive charge attracting negatively charged atoms. Hydrogen bond however is quite a weak type of bond having a bond energy of only 4 to 10 K-cal. as against 50 to 100 K-cal for ordinary covalent bonds.

Exercises

1. Write short notes on (i) atomic number, (ii) isotopes, (iii) valence electrons, (iv) electronic formula, (v) resonance, and (vi) hydrogen bond.

2. Give an account of the modern views regarding valency.

3. Write a short essay on variable valency as explained in the theory of atomic structure. Clearly explain what you understand by electro-valency and covalency.

4. Write a short essay on Dalton's atomic theory in the light of modern discoveries in physical science.

5. What is meant by the atomic number of an element? Discuss the statement that the atomic number of an element is more fundamental than its atomic weight. How is the atomic number of an element determined.

6. Write the electron dot formula for each of the following covalent compounds :—(a) $CHCl_3$, C_3H_6, H_2S, Na_2O, (b) $LiCl$, CaO, $KMgF_3$, and BH_4^- ion, S_3^- ion, O_2^- ion, NH_4^+ ion.

7. From Lewis idea of covalency give an explanation for the fact that interhalogens contain an even number of atoms in a molecule, whereas polyhalide ions contain an odd number.

THE END

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